The MAP3S Precipitation Chemistry Network:

Ninth Periodic Summary Report (1985)

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THE MAP3S NETWORK DATA AND QUALITY
CONTROL SUMMARY FOR 1985

M. Terry Dana

February 1988

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PREFACE

This report is the ninth in a series of periodic summary reports of the MAP3S precipitation Chemistry Network (PCN). Beginning with this issue, summaries of data analyses and quality control activities are included; complete data listings are available via quarterly reports and through the Atmospheric Deposition System (ADS). Data users who wish to make their own summary analyses are encouraged to consult the documentation that accompanies complete data listings; any doubts about the format, units, or validity of data entries should be resolved through consultation with ADS managers or the author.

A great number of persons have contributed to the operation of the PCN and interpretation of results over the 10 years of the network's history; their efforts are greatly appreciated, but space permits listing only those active during the period from 1985 to the present writing:

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University of Virginia Department of Environmental Sciences	James Galloway Linda Jolley Bill Keene Mark Castro Connie Gold Cindy Donoghue

EXECUTIVE SUMMARY

This report, the ninth in a series documenting results from the MAP3S Precipitation Chemistry Network, contains a statistical summary of daily precipitation chemistry data from the nine-site network in the eastern United States, both for the year 1985 alone and for the period 1977 through 1985. In addition, a report on quality control and external quality assurance activities is included, which updates the 1980 quality control report.

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1.0 INTRODUCTION

The MAP3S Precipitation Chemistry Network (PCN) has been in operation since 1976, collecting event and daily wet-only samples, conducting chemical analyses, and reporting the results through quarterly data listings, summary reports, and electronic data transfer to the Atmospheric Deposition System (ADS) data base.⁽¹⁾ Chemical analyses for the network were sponsored in 1985 by the U.S. Environmental Protection Agency; they are currently sponsored by the Environment, Health and Safety Research Program Office of U.S. Department of Energy. Pacific Northwest Laboratory's (PNL) responsibilities are site maintenance and auditing, chemical and data analyses, and reporting. The site operations are funded by separate contracts with the cooperating organizations listed in the Preface.

The PCN consists of nine sites (the number has remained constant since 1981) located in the eastern half of the continental United States. Figure 1 is a map showing the locations of the sampling sites, and Tables 1 and 2 list

FIGURE 1. Locations of the MAP3S Precipitation Chemistry Network Sites

TABLE 1. Network Site Identification and Participating Organizations

Site Number	Site Name	Participating Organization
1	Whiteface	Atmospheric Sciences Research Center State University of New York at Albany
2	Ithaca	Section of Ecology and Systematics Cornell University
3	Penn State	Department of Meteorology Pennsylvania State University
4	Virginia	Department of Environmental Sciences University of Virginia
5	Illinois	Illinois State Water Survey Champaign, Illinois
6	Brookhaven	Atmospheric Sciences Division Brookhaven National Laboratory
7	Lewes	College of Marine Studies University of Delaware
8	Oxford	Institute of Environmental Sciences Miami University
9	Oak Ridge	Oak Ridge National Laboratory

TABLE 2. Network Site Details

Site Number	Name	Location		Elevation (m, msl)	Date of First Sample Collected
		Longitude	Latitude		
1	Whiteface	73° 51'	44° 23'	605	October 11, 1976
2	Ithaca	76° 43'	42° 23'	503	October 26, 1976
3	Penn State	77° 57'	40° 47'	396	September 22, 1976
4	Virginia	78° 32'	38° 2'	171	December 12, 1976
5	Illinois	88° 22'	40° 3'	213	November 20, 1977
6	Brookhaven	72° 53'	40° 52'	24	February 9, 1978
7	Lewes	75° 0'	38° 46'	0	March 1, 1978
8	Oxford	84° 44'	39° 32'	283	October 1, 1978
9	Oak Ridge	84° 17'	35° 58'	330	January 7, 1981

organizational and location details. More details on the network operation may be found in open-literature publications,^(2,3) a quality control report,⁽⁴⁾ and past periodic summary reports (PSR).⁽⁵⁻¹²⁾ The seventh in the latter series contains a history of the PCN (through 1983), a bibliography of publications that have employed PCN data, and the most recent detailed summary of quality control activities.

A major objective of the PCN is chemical analysis of precipitation samples for the major ionic species. Table 3 is a list of the species, methods, instruments, detection limits, and goals for measurement uncertainty. Over the course of 10 years of operation, several analysis methods have changed, as have basic detection limits and estimated errors. Shown in the table are current methods and typical values for the variables. Past laboratory specifications may be found in the previous PSRs; a chronology of relevant network changes, including those involving field practices and collector equipment, may also be found in the ADS data base (for source, see the Preface).

Beginning with this issue (the ninth), the format of the PSR changes to an annual summary of data analyses for the current year and all previous years and quality control activities. Complete data listings (including hourly precipitation amounts) continue to be available via the quarterly reports, from the author or other PNL persons listed in the Preface, or from the ADS. The hourly precipitation amount data, which are presently totaled for precipitation events within the chemistry listings, are being integrated with the chemistry data base; it is expected that more detailed event-summaries of precipitation will be available in future periodic reports.

Section 2 considers quality control procedures and analyses of laboratory and field performance; this summary is intended as a replacement for the earlier quality control report.⁽⁴⁾ Section 3 is a data summary for 1985 and for the period 1977 through 1985, updating past summaries in PSRs and the journal articles.^(2,3) Section 4 describes the 1985 results from the external quality assurance, blind sample program administered by the U.S. Geological Survey.

TABLE 3. Chemical Species and Analysis Details

Species	Method ^(a)	Instrument	Minimum Detection Limit (μM) ^(b)	Quantitative Detection Limit (μM) ^(c)	Estimated Error ^(d)
H ⁺ (free)	Electrode	Corning® Model 135 pH/Ion Meter	--	--	± 0.05 pH units ^(e)
Conductivity	Bridge	Markson Electro- mark®	1.20	--	$\pm 20\%$
SO ₃ ⁼	AWC	Alpkem® Auto Analyzer	0.10	0.20	± 60 (QDL or 10%)
SO ₄ ⁼	IC	Dionex™ System 2000i (Anion)	0.03	0.20	± 60 (QDL or 10%)
NO ₃ ⁻	IC	Dionex™ System 2000i (Anion)	0.05	0.20	± 60 (QDL or 10%)
Cl ⁻	IC	Dionex™ System 2000i (Anion)	0.50	2.00	± 60 (QDL or 10%)
PO ₄ ³⁻	IC	Dionex™ System 2000i (Anion)	0.05	0.20	± 60 (QDL or 10%)
NH ₄ ⁺	IC	Alpkem® Auto Analyzer	0.10	0.50	± 60 (QDL or 10%)
Na ⁺	ICAP	Leeman Labs Plasma- Spec®. ICP 2.5	0.10	0.40	± 60 (QDL or 10%)
K ⁺	ICAP	Leeman Labs Plasma- Spec®. ICP 2.5	0.20	0.50	± 60 (QDL or 10%)

TABLE 3. (contd)

Species	Method ^(a)	Instrument	Minimum Detection Limit (μM) ^(b)	Quantitative Detection Limit (μM) ^(c)	Estimated Error ^(d)
Ca ⁺⁺	ICAP	Leeman Labs Plasma-Spec . ICP 2.5	0.05	0.20	$\pm$ GO(QDL or 10%)
Mg ⁺⁺	ICAP	Leeman Labs Plasma-Spec . ICP 2.5	0.08	0.20	$\pm$ GO(QDL or 10%)

(a) AWC = Automated Wet Chemistry; IC = Ion Chromatography; ICAP = Inductively Argon Coupled Plasma.

(b) Concentrations are expressed in molar units: $\mu\text{M} = \mu\text{mol}/\text{L}$.

(c) Best obtained--Some analysis sessions result in higher maximum detection limits. These are noted, where relevant, in the Appendix.

(d) GO = Greater Of; QDL = Quantitative Detection Limit.

(e) At pH = 4.

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1/1/20	10:00	New York	Cash	\$100.00	\$100.00
1/1/20	10:00	New York	Cash	\$100.00	\$100.00
1/1/20	10:00	New York	Cash	\$100.00	\$100.00
1/1/20	10:00	New York	Cash	\$100.00	\$100.00
1/1/20	10:00	New York	Cash	\$100.00	\$100.00
1/1/20	10:00	New York	Cash	\$100.00	\$100.00
1/1/20	10:00	New York	Cash	\$100.00	\$100.00
1/1/20	10:00	New York	Cash	\$100.00	\$100.00
1/1/20	10:00	New York	Cash	\$100.00	\$100.00
1/1/20	10:00	New York	Cash	\$100.00	\$100.00
1/1/20	10:00	New York	Cash	\$100.00	\$100.00

2.0 QUALITY CONTROL

2.1 INTRODUCTION

Quality control (QC) and quality assurance (QA) for PCN are administered under a formal QA plan; since PCN has existed through much of its history under the sponsorship of the U.S. Environmental Protection Agency (EPA), the QA plan in force is of the EPA format. Integral to the plan is the inclusion of "quality control descriptors" (QCD), which constitute standard operating procedures for the project. Appendix A contains a list of these QCDs and summaries of their content. Additional details or copies may be obtained from the author.

Quality control procedures for MAP3S/PCN have been documented in a previous report;⁽⁴⁾ that report summarized procedures for site selection and verification, for field equipment and sampling, and for the laboratory. Site selection and verification procedures [like those in force for the National Atmospheric Deposition Program (NADP) and National Trends Network (NTN)] have not changed. Equipment quality control procedures have been modified to account for change of the precipitation sampler type to the Aerochem Metrics (ACM) and the rain gauge to the Belfort weighing type. Since these equipment types are now standard for both PCN and NADP/NTN, procedures for equipment quality control are documented elsewhere.⁽¹³⁾ The QC portion of this report will accordingly deal with field sampling and laboratory analysis procedures.

The following subsections provide quality control data and analyses relating to the procedures described in the QCDs for field sampling and laboratory analysis. Some QC analyses include data from 1984 as well as 1985, since these have not been previously reported. External QA, by means of blind audit sample analyses provided by the U.S. Geological Survey, is dealt with in Section 4.

2.2 FIELD PROCEDURES

As noted in Section 1, the PCN project at PNL is responsible for administering quality control for the network sites, which are funded separately by DOE. The primary tasks involved are provision of a site operator's manual and the conduct of periodic (nominally annual) site audits. The manual, which

is one of the PCN project's QCDs (Appendix A), contains procedures for testing field pH measurements and for collecting field blank samples. The latter are designed to estimate blank contributions to chemical concentrations. The following paragraphs summarize results of these activities during 1984 and 1985.

2.2.1 Field Blanks

The effect of dry deposition, collector malfunction, or other non-precipitation contributions (such as operator contamination) on the chemistry of PCN samples is estimated by collection and analysis of dry-bucket samples. At the end of approximately one week without measurable precipitation, the collector bucket is replaced as if a precipitation sample had been collected. A volume (approximately 250 ml) of deionized water, provided to the sites by the Precipitation Chemistry Laboratory (PCL) at PNL, is added to the bucket and allowed to stand overnight or at least two hours. Thereafter, the water is treated exactly like a precipitation sample, except that a special identification is used and the sample is returned in the original field blank water bottle. At PCL, a normal chemical analysis is performed.

The mass of each chemical species found in the field blank sample represents an estimate of the non-precipitation contribution to the sample for that species. The simplest measure of the field blank effect is an average, over the number of field blank samples for a period (in the present case, 1984 and 1985), percent contribution to concentration (or deposition) for an average week. This percent R is calculated as follows:

$$R = \frac{C_B V_B}{C_W V_W} \times 100 \quad (1)$$

where C_B and V_B are the average concentration and volume of the field blank samples, C_W is the average annual concentration for the species for the site, and V_W is the annual average weekly volume of sample. Table 4 lists the R values and input to Equation (1) for the field blank samples collected during 1984 and 1985. Also shown are the numbers of field blanks collected, the average field blank masses, and the estimated average concentration contributed to a week's precipitation. Since many of the field blank concentrations

TABLE 4. Field Blank Masses, Volumes, and Percent Contribution to Annual Average Weekly Concentrations, 1984 and 1985: Upper Limit (less than MDL taken as MDL).

SITE	N	VW	VB	SO ₄					NO ₃				
				MB	CB	CW	CBW	R, %	MB	CB	CW	CBW	R, %
WH	4	1.37	0.23	0.14	0.63	20	0.10	0.52	0.29	1.30	18	0.21	1.21
IT	5	1.44	0.24	0.69	2.88	29	0.48	1.65	0.75	3.30	26	0.55	2.11
PS	7	1.42	0.20	0.12	0.61	30	0.08	0.28	0.18	0.82	27	0.11	0.42
VA	15	1.43	0.22	0.44	2.00	23	0.30	1.33	0.32	1.43	20	0.22	1.10
IL	1	1.01	0.25	0.40	1.60	26	0.39	1.52	0.62	2.70	24	0.66	2.78
BR	1	1.84	0.21	0.48	2.30	18	0.26	1.45	0.52	2.30	15	0.26	1.75
LE	22	1.47	0.20	0.47	2.37	25	0.32	1.28	0.79	3.45	18	0.46	2.60
OX	9	1.25	0.24	0.45	1.86	27	0.35	1.32	0.29	1.29	22	0.24	1.12
OR	9	1.66	0.24	0.26	1.09	22	0.15	0.71	0.34	1.48	15	0.21	1.42

Cl				H					NH ₄				
CB	CW	CBW	R, %	MB	CB	CW	CBW	R, %	MB	CB	CW	CBW	R, %
2.43	3.4	0.41	12.0	0.67	2.92	44	0.49	1.11	0.11	0.50	11	0.08	0.76
2.48	4.2	0.41	9.84	1.05	4.60	67	0.76	1.14	0.11	0.50	16	0.08	0.52
2.04	5.6	0.29	5.13	0.71	3.11	73	0.43	0.60	0.17	0.74	13	0.10	0.80
3.24	9.0	0.50	5.54	1.20	5.24	52	0.80	1.55	0.20	0.90	13	0.14	1.07
2.50	4.1	0.62	15.1	0.23	1.00	51	0.24	0.49	0.41	1.80	15	0.45	2.97
2.00	37	0.23	0.62	1.33	5.80	40	0.66	1.65	0.36	1.60	6.8	0.18	2.69
5.80	90	0.79	0.88	1.96	8.55	47	1.16	2.48	0.33	1.44	12	0.20	1.63
2.48	5.0	0.48	9.52	1.03	4.49	53	0.86	1.63	0.36	1.59	16	0.31	1.91
1.23	5.3	0.18	3.36	0.90	3.92	43	0.56	1.32	0.15	0.69	8.4	0.10	1.19

Na				Ca					Mg				
CB	CW	CBW	R, %	MB	CB	CW	CBW	R, %	MB	CB	CW	CBW	R, %
0.9	2.0	0.14	7.1	0.34	1.5	1.8	0.25	14.0	0.11	0.5	0.5	0.08	16.7
0.8	1.4	0.13	9.29	0.25	1.1	2.3	0.18	8.0	0.11	0.5	0.6	0.08	13.8
0.8	2.6	0.10	4.12	0.25	1.1	2.5	0.15	6.2	0.11	0.5	0.5	0.07	14.0
1.2	5.5	0.18	3.36	0.41	1.8	1.8	0.27	15.4	0.11	0.5	0.9	0.07	8.54
4.2	2.5	1.03	41.6	0.52	2.3	5.5	0.56	10.4	0.32	1.4	1.1	0.34	31.5
3.2	32	0.36	1.14	0.08	0.4	1.7	0.03	2.3	0.11	0.5	3.4	0.05	1.67
4.0	76	0.54	0.72	0.27	1.2	3.2	0.16	5.1	0.11	0.5	7.6	0.06	0.89
1.1	2.5	0.21	8.45	0.25	1.1	4.1	0.21	5.2	0.11	0.5	0.8	0.09	12.0
0.6	2.9	0.08	2.99	0.23	1.0	3.8	0.14	3.8	0.11	0.5	0.8	0.07	9.03

TABLE 4. (contd)

SITE	N	VW	VB	K					Conductivity				
				MB	CB	CW	CBW	R, %	MB	CB	CW	CBW	R, %
WH	4	1.37	0.23	0.23	1.0	2.4	0.16	7.0	0.48	2.1	21	0.35	1.7
IT	5	1.44	0.24	0.16	0.7	1.5	0.12	8.1	0.71	3.1	32	0.51	1.6
PS	7	1.42	0.20	0.15	0.7	2.1	0.09	4.5	0.57	2.5	33	0.35	1.1
VA	15	1.43	0.22	0.21	0.9	2.4	0.14	5.9	0.57	2.5	25	0.38	1.5
IL	1	1.01	0.25	0.11	0.5	2.0	0.12	6.2	0.73	3.2	26	0.79	3.0
BR	1	1.84	0.21	0.23	1.0	3.2	0.11	3.6	0.80	3.5	23	0.39	1.7
LE	22	1.47	0.20	0.16	0.7	2.5	0.09	3.8	1.03	4.5	34	0.61	1.8
OX	9	1.25	0.24	0.11	0.5	2.0	0.09	4.8	0.50	2.2	26	0.42	1.6
OR	9	1.66	0.24	0.11	0.5	--	0.07	--	0.59	2.6	22	0.37	1.7

LEGEND:

N	Number of field blank samples
VW	Average weekly precipitation volume (ℓ)
VB	Average volume of blank solution (ℓ)
MB	Average mass in blank (μM)
CB	Average concentration of blank solution (μM)
CW	Annual average sample concentration (μM)
CBW	Average blank concentration in sample (μM)
R	Contribution to average weekly deposition (%)

measured are at or below detection limits, an upper limit on the estimate has been made by assuming that the below-minimum detection limit (MDL) values are actually equal to MDL.

This field blank contribution estimate is a very rough approximation, for several reasons. Implicit in the calculation is the assumption that the blank contribution during rainfall is the same as that during dry periods, but the dry-period contribution is what is actually measured. The site operator's handling of the sample differs somewhat from that for an actual precipitation sample, so the contribution by operator contamination may not be adequately determined. Additional factors possibly not properly accounted for are the blank effect on individual samples, whose volume may be considerably less than that for an average week, and the effect of the number of days of exposure during an individual sample.

These individual sample effects can be estimated by considering the distributions of sample time, volume, and concentration, and deriving a distribution of field blank contribution. This procedure uses the general statistical analysis program described in Section 3, acting on percent field blank contributions R_i for events:

$$R_i = \frac{M_B D_i}{7C_i V_i} \times 100 , \quad (2)$$

where M_B is the average field blank mass (Table 4), D_i is the sample time in days, and V_i and C_i are the volume and concentration of the species of interest in the sample. The subscript i refers to an individual sample. If D_i is more than one, two, etc., weeks (i.e., 7, 14, ... days), the value of D_i is replaced by D_i-7 , D_i-14 , etc. The resulting statistics for R_i are listed in Table 5, for those sites that had 5 or more field blank samples during 1984 and 1985. The distributions provide an assessment of the potential field blank effect (albeit still approximate due the use of a single field blank mass contribution to all samples) on the distribution of event volumes and concentrations. These distributions are illustrated in Figure 2, which has log-probability plots for the species Ca and S. There is no systematic difference between the sites in the field blank distribution behavior, so a simple average for the six sites is shown; individual site plots may be drawn from the data in Table 5. Calcium and sulfur are plotted, because they represent the extremes among the species; for example, about 98% of the events have field blank contributions less than 10% for S, but for Ca, the value is 60%. The distribution statistics, while still showing that field blank contributions are generally unimportant, do demonstrate (unlike the week-average figures in Table 4) that for some individual events (predominantly those with low volumes and thus low overall deposition) the potential field blank effect can be large.

2.2.2 Collection Efficiency

One measure of the effective operation of the automatic precipitation collector is the collection efficiency. This is calculated as the ratio of the sample volume collected to the volume expected on the basis of the rain

TABLE 5. Distribution Statistics for Percent Contribution of Field Blank to Concentration or Deposition: Sites with 5 or More Field Blank Samples, 1984 and 1985

	SITE	N	NEDT	AME	ASD	GME	GSD	MIN	Percentage of Samples					MAX
									5	25	50	75	95	
S	IT	171	158	4.1	6.2	1.79	4.6	0	0.19	0.83	1.94	4.28	13.7	41.9
	PS	211	180	1.2	4.8	0.25	6.6	0	0.01	0.13	0.25	0.69	3.6	59.1
	VA	127	94	2.2	5.5	0.63	6.2	0	0.00	0.31	0.66	1.61	7.7	46.6
	LE	126	106	2.6	4.9	0.65	10.0	0	0.00	0.31	0.87	2.68	9.1	29.0
	OX	181	152	2.8	6.3	1.00	5.5	0	0.01	0.49	1.05	2.46	5.9	57.2
	OR	133	130	1.2	3.4	0.23	12.3	0	0.00	0.13	0.44	0.92	3.4	32.0
NO ₃	IT	171	158	3.1	4.4	1.53	4.3	0	0.20	0.83	1.81	3.23	9.2	34.9
	PS	211	180	0.8	1.8	0.30	5.6	0	0.00	0.17	0.35	0.74	2.8	21.6
	VA	127	94	1.0	1.3	0.43	5.2	0	0.00	0.23	0.46	1.07	3.8	6.4
	LE	126	106	4.5	8.8	1.17	9.9	0	0.00	0.63	1.50	4.80	18.3	71.6
	OX	181	152	1.3	1.3	0.65	5.0	0	0.00	0.34	0.75	1.80	3.9	6.6
	OR	133	130	1.5	3.9	0.36	11.5	0	0.00	0.24	0.79	1.42	3.4	41.1
Cl	IT	171	158	16.4	27.5	7.4	4.8	0	0.25	3.95	8.3	17.1	43.6	207
	PS	211	180	11.6	21.8	4.5	6.1	0	0.02	2.56	5.5	10.5	41.0	206
	VA	127	94	9.1	11.1	4.0	5.7	0	0.02	1.99	4.6	11.6	30.4	48
	LE	126	107	8.4	14.9	1.6	12.4	0	0.00	0.52	2.4	7.5	39.2	77
	OX	181	152	13.4	13.0	6.6	5.4	0	0.03	3.48	9.0	20.1	34.6	62
	OR	133	130	4.7	7.8	1.1	12.5	0	0.00	0.60	1.9	4.7	19.2	42
H	IT	171	158	6.6	42.2	1.3	5.0	0	0.15	0.61	1.5	2.75	11.7	525
	PS	211	176	2.5	9.8	0.6	6.2	0	0.01	0.35	0.7	1.63	9.0	122
	VA	127	94	2.3	3.8	0.8	5.6	0	0.00	0.41	0.9	2.04	9.5	20
	LE	126	106	9.0	23.7	1.7	10.0	0	0.00	0.78	2.0	6.32	35.8	143
	OX	181	152	2.9	4.5	1.2	5.6	0	0.01	0.59	1.4	2.96	9.5	29
	OR	133	129	2.1	7.0	0.4	13.3	0	0.00	0.28	0.8	1.68	5.7	75
NH ₄	IT	171	155	2.4	9.1	0.6	5.9	0	0.05	0.27	0.6	1.41	6.6	94
	PS	211	174	2.8	7.2	0.7	7.1	0	0.00	0.30	0.7	2.37	8.7	72
	VA	127	92	5.4	32.6	0.5	8.6	0	0.00	0.20	0.5	1.35	10.9	312
	LE	126	107	6.3	25.7	1.0	11.3	0	0.00	0.35	1.4	3.97	15.5	255
	OX	181	150	5.7	17.9	1.5	6.3	0	0.02	0.60	1.5	4.26	15.2	181
	OR	133	129	3.2	11.1	0.4	13.8	0	0.00	0.15	0.6	1.82	9.9	112
Na	IT	171	154	20.9	31.6	8.3	5.6	0	0.31	4.04	9.4	22.6	79	226
	PS	211	169	15.4	37.0	5.1	7.1	0	0.01	2.88	6.2	14.0	47	432
	VA	127	91	12.6	32.1	3.4	6.6	0	0.01	1.25	4.4	9.5	45	265
	LE	126	105	9.4	18.6	1.5	14.0	0	0.00	0.48	2.0	7.5	55	109
	OX	181	144	14.4	16.3	6.8	5.2	0	0.05	3.70	9.3	17.7	49	79
	OR	133	125	5.5	9.6	1.0	14.7	0	0.00	0.38	1.8	5.8	26	

TABLE 5. (contd)

	SITE	N	NEDT	AME	ASD	GME	GSD	MIN	Percentage of Samples					
									5	25	50	75	95	MAX
Ca	IT	171	152	23.8	46.1	8.2	5.6	0	0.38	3.62	9.3	23.4	102	447
	PS	211	173	16.4	24.9	5.8	6.6	0	0.07	2.42	6.8	19.9	61	181
	VA	127	91	33.3	64.0	10.9	6.1	0	0.06	5.32	12.0	23.9	115	469
	LE	126	104	14.7	21.7	4.3	10.6	0	0.01	2.66	6.9	18.1	51	144
	OX	181	145	15.1	32.1	5.7	5.2	0	0.18	2.94	6.0	13.9	55	293
	OR	133	126	8.4	17.7	1.6	12.3	0	0.01	0.81	2.6	7.5	41	157
Mg	IT	171	153	31.8	74.3	12.3	5.2	0	0.58	6.22	14.4	30.3	101	839
	PS	211	173	26.7	43.4	9.6	7.0	0	0.04	4.15	12.9	27.1	87	381
	VA	127	91	16.7	25.2	6.9	5.6	0	0.05	3.14	8.6	19.4	52	172
	LE	126	104	7.1	13.0	1.3	13.7	0	0.00	0.47	2.0	7.0	32	82
	OX	181	145	18.5	24.8	8.7	5.0	0	0.12	4.41	9.1	23.2	53	176
	OR	133	126	14.9	28.7	3.1	12.9	0	0.01	1.70	5.9	13.4	54	211
K	IT	171	152	71.6	154	24.9	5.1	0	1.28	11.3	27.0	58.5	266	1060
	PS	211	169	54.5	82	18.8	6.6	0	0.18	7.6	26.1	62.9	180	503
	VA	127	91	39.5	75	11.8	6.6	0	0.05	4.7	10.9	36.1	114	486
	LE	126	106	36.1	112	6.1	12.1	0	0.01	2.4	11.6	26.8	108	937
	OX	181	144	37.0	61	13.9	5.6	0	0.15	6.6	15.2	39.1	127	444
	OR	133	125	31.3	65	5.0	14.9	0	0.01	1.9	10.1	26.6	126	369
Conductivity	IT	171	155	2.9	3.6	1.4	4.3	0	0.18	0.79	1.8	3.1	10.6	20
	PS	211	172	2.1	3.3	0.9	5.6	0	0.01	0.54	1.0	2.3	7.9	21
	VA	127	94	1.8	2.8	0.7	5.5	0	0.00	0.37	0.8	1.6	7.9	15
	LE	126	104	3.3	5.5	1.0	9.3	0	0.00	0.53	1.7	3.2	9.1	42
	OX	181	150	2.1	2.7	1.0	5.3	0	0.01	0.51	1.2	2.5	6.7	16
	OR	133	126	1.6	2.3	0.4	12.3	0	0.00	0.26	0.9	1.9	4.5	14

LEGEND:

N	Number of field blank samples
NEDT	Number of samples after editing for valid analyses
AME	Arithmetic mean
ASD	Standard deviation about arithmetic mean
GME	Geometrical mean
GSD	Geometrical standard deviation
MIN	Minimum
MAX	Maximum

FIGURE 2. Log-Probability Plot of Estimated Percent Field Blank Contribution for S and Ca: 1984 and 1985 Field Blank Data

gauge precipitation amount for the event. Distribution statistics for collection efficiency are tabulated in Section 3. It should be noted that collection efficiencies need not necessarily be less than unity; under certain wind and precipitation conditions, the bucket of the automatic sampler may be a more efficient collector. Because this variability is not generally subject to the site operator's control, the collection efficiency is used only as an indicator of potential problems with either the collector or the rain gauge. Over the network history, such problems (primarily with the rain gauge) have been identified, and the time limits for the error are known; however, the data base for collection efficiency has not been adjusted, so the distribution statistics shown in Section 3 include these errors.

2.2.3 pH Tests and Lab-Field pH Difference

The measurement of pH in the field provides an important quality control function, because great differences in pH between the field and the laboratory offer evidence for contamination, both before and after field pH analysis. Field pH values also offer evidence of real chemical changes in samples during the time between collection and analysis, but this is only a rough indicator, since pH measurements are uncertain without accompanying measurements of sufficient other ions to determine ion balance. At any rate, a suitable level of quality control on field pH measurements is provided through periodic test measurements of samples provided by PCL, and through statistical analysis of the lab-field pH differences.

The test samples for field pH consist of aliquots of the PCL quality control sample solution (used by PCL for determining precision and checking accuracy), or selected excess past samples, shipped approximately quarterly to the sites (and also accompanying site audits; see Section 2.2.4, below). The site operators treat the aliquots as precipitation samples, report results, and return the sample for possible reanalysis by PCL. Statistics on pH test samples are not maintained, but, on receipt at PCL, comparisons are made between expected and measured values, and corrective action is taken (including resubmission of a test sample to a site) when necessary.

Analyses of lab-field pH difference serve a useful purpose (despite the inherent unmeasurable uncertainty in the field values), in that spatial (and possibly temporal) trends in the chemistry of precipitation may be indicated.

These trends may result from reactions after collection and before analysis. Temporal trends in the difference at given sites may be an indication of the quality of measurements at the site, especially before the institution of pH testing. Statistics on lab-field pH difference are presented in Section 3.

2.2.4 Site Audits

Personnel familiar with PCN and precipitation chemistry sampling in general, from PCL or other groups at PNL, visit the network sites periodically. When practical, site visits are accomplished annually. The visit includes an observation of all activities covered by the site operator's manual, discussions with the site operators and managers when problems are identified, and corrective actions taken. A comprehensive form is filled out and reported with periodic PCN reports; a sample copy of this form is provided in Appendix D. As a result of personnel availability problems, no site audits were conducted during 1985; the most recent documentation of site audits appears in the eighth PSR.⁽¹²⁾

2.3 LABORATORY PROCEDURES

The QA plan for PCN dictates formal procedures for assuring quality chemical analyses. The most important among these include: specification of goals for accuracy, precision, and representativeness; performance of tests to assess if the above goals are met; documentation of sample identification, custody, and performance regarding the quality goals; assurance of comparability of measurements when techniques change; and procedures for corrective action. The quality goals are listed in Table 3 (Section 1), and the previous QC report⁽⁴⁾ describes sample identification and maintenance. This section deals with the tests of laboratory quality, including definitions of quality-related calculated parameters, and statistics on recent laboratory performance.

2.3.1 Accuracy, Precision, and Bias

Accuracy is defined as the difference between a measured value and a known true value. Often the measured value is a mean of a number of determinations; thus accuracy includes precision, which is the degree of agreement between repeated measurements. Bias is defined as a systematic positive or negative difference between a measured value and the true value.

Accuracy of the PCL measurements is estimated by analysis of quality control sample results. The quality control samples are solutions of known concentration (either externally provided or prepared, as with calibration standards, from National Bureau of Standards (NBS) traceable standard chemicals) that are analyzed as unknowns once per every 10 PCN samples (once per every 5 PCN samples for the ion chromatograph species). For a given species, for N runs of the QC sample, the percent accuracy A is defined as

$$A = \frac{\text{Mean } (|K-M|)}{\text{Mean } (K)} \times 100 \quad (3)$$

where M is the measured value and K is the known value. Similarly calculated is bias, with the numerator the actual difference (positive or negative):

$$B = \frac{\text{Mean } (K-M)}{\text{Mean } (K)} \times 100 \quad (4)$$

Precision, which does not require knowledge of the true value of the concentration, but only the reproducibility of the measurement technique, is defined as the coefficient of variation (standard deviation/mean) of the N measurements of the sample. Precision data can be obtained from repeated measurements of any sample (in fact the QA plan requires reanalysis of one in twenty PCN samples), but for present purposes the QC sample data are used.

In principle, accuracy, precision, and bias vary from analysis session to analysis session (any period for which a single calibration is applicable); therefore, these quantities were determined separately for separate analysis days. Results for a recent (during 1985 and 1986) number of non-sequential analysis sessions are listed in Table 6. Also shown in the table are values for a number of days combined (including days with only one or two QC sample runs, which are not listed separately in the table; thus, the last N value for a species may be greater than the sum of the other N values), and simple averages of all the species values. Hydrogen ion data are listed in two groups; one for measurements during a period of biased measurements (see below), and one more recently after corrective action. Figure 3 is a comparison of the

TABLE 6. Accuracy, Precision, and Bias Data for Selected Analysis Sessions -- 1985 and 1986

SPECIES	DAY	N	MEANS				STD DEV OBS	%		
			CSTD	COBS	DIFF	ABSD		ACC.	BIAS	PREC.
SO ₂	1	9	3.0	3.1	0.09	0.15	0.18	5.09	2.94	5.89
	2	9	3.0	2.9	-0.07	0.10	0.10	3.42	-2.38	3.45
	3	7	3.2	3.1	-0.10	0.11	0.12	3.45	-3.08	4.03
	*	25						4.02	-0.70	5.23
SO ₄	1	8	32	32	-0.85	1.01	0.87	3.13	-2.63	2.75
	2	13	32	32	-0.50	0.60	0.53	1.87	-1.56	1.67
	3	4	32	33	0.15	0.50	0.50	1.55	0.46	1.54
	*	35						2.68	-1.01	3.70
NO ₃	1	8	69	67	-2.17	2.73	2.82	3.96	-3.15	4.22
	2	13	69	67	-2.38	2.39	1.22	3.47	-3.46	1.83
	3	4	69	69	-2.72	2.72	0.50	3.95	-3.94	0.73
	*	35						3.36	-2.92	2.79
Cl	1	8	16	16.0	-0.16	0.43	0.59	2.69	-0.98	3.65
	2	14	16	16.0	-0.19	0.42	0.60	2.62	-1.19	3.76
	3	4	16	17.2	-1.36	1.36	0.29	8.58	-8.58	1.66
	*	36						11.5	-10.1	13.0
PO ₄	1	8	36	35.3	0.59	1.61	1.73	4.48	1.64	4.90
	2	14	36	34.9	0.98	1.09	0.82	3.03	2.72	2.35
	3	5	36	35.8	0.07	0.36	0.46	1.00	0.21	1.30
	*	37						3.15	1.60	3.17
H	1	12	44	38.2	5.45	5.45	2.92	12.5	12.5	7.6
	2	11	44	21.8	21.81	21.81	7.90	50.0	50.0	36.2
	3	9	44	26.1	17.58	17.58	6.40	40.3	40.3	24.5
	*	32						34.2	34.2	22.8
H	4	10	41	39.9	0.83	0.83	0.80	2.04	2.04	2.01
	*	26	44	47.8	4.11	4.78	4.89	10.9	9.43	10.2
COND	1	12	20	20.2	-0.17	0.28	0.33	1.42	-0.83	1.65
	2	11	20	20.2	-0.18	0.40	0.48	2.00	-0.91	2.37
	3	9	20	19.8	0.16	0.44	0.60	2.22	0.78	3.02
	*	32						1.88	-0.32	2.34
NH ₄	1	8	38	37.8	0.28	0.33	0.32	0.85	0.72	0.85
	2	15	21	19.8	1.04	1.04	0.49	4.98	4.98	2.46
	3	11	21	20.9	-0.07	1.01	1.26	4.86	-0.35	6.05
	4	15	21	21.4	-0.55	0.83	0.86	4.01	-2.66	4.02
	*	49						3.67	0.67	3.35

TABLE 6. (contd)

SPECIES	DAY	N	MEANS				STD DEV OBS	%		
			CSTD	COBS	DIFF	ABSD		ACC.	BIAS	PREC.
Na	1	5	218	218.2	-0.20	2.20	2.93	1.01	-0.09	1.34
	2	14	218	214.2	3.79	8.21	9.77	3.77	1.74	4.56
	3	7	43	41.5	1.87	1.87	0.85	4.31	4.31	2.05
	4	6	43	43.3	-0.33	2.67	2.81	6.20	-0.78	6.48
	5	9	108	108.3	-0.29	2.29	2.91	2.12	-0.26	2.69
	*	41						3.48	0.98	3.43
K	1	5	128	126.0	2.00	4.40	5.10	3.44	1.56	4.05
	2	14	128	126.9	1.07	13.64	17.24	10.66	0.84	13.59
	3	7	25	23.4	1.97	2.03	1.35	7.99	7.76	5.74
	4	6	25	23.0	2.00	2.00	1.41	8.00	8.00	6.15
	5	7	64	64.0	-0.50	3.50	3.70	5.51	-0.79	5.79
	*	39						7.12	3.47	7.06
Ca	1	9	25	25.1	-0.11	0.11	0.31	0.44	-0.44	1.25
	2	6	25	24.8	0.17	0.17	0.26	0.67	0.67	1.06
	3	11	25	24.9	0.10	0.41	0.49	1.64	0.40	1.97
	4	14	25	24.6	0.40	0.46	0.40	1.83	1.60	1.64
	5	5	25	24.6	0.38	0.38	0.42	1.52	1.52	1.69
	*	45						1.22	0.75	1.52
Mg	1	9	41	41.0	0.00	0.44	0.82	1.08	0.00	1.99
	2	6	41	40.7	0.33	0.93	1.05	2.28	0.81	2.58
	3	11	41	41.1	-0.08	0.81	0.94	1.97	-0.20	2.29
	4	14	41	40.8	0.16	0.61	0.69	1.48	0.40	1.70
	5	5	41	40.2	0.76	0.76	0.75	1.85	1.85	1.87
	*	45						1.73	0.57	2.09

LEGEND:

DAY	Arbitrary analysis session date number
*	Composite of several analysis sessions - may contain single standard run sessions not included within "DAYS"
N	Number of QC standard runs
CSTD	QC standard concentration (μM)
COBS	Mean observed concentration (μM)
DIFF	Difference (CSTD - COBS)
ABSD	Absolute difference
STD DEV OBS	Observed standard deviation
ACC.	(ABSD/CSTD) x 100
BIAS	(DIFF/CSTD) x 100
PREC.	(STD DEV COBS/COBS) x 100

FIGURE 3. Accuracy, Bias, and Precision Estimates for PCL Analyses from Recent (see text) QC Check Sample Data

accuracy, bias, and precision results for all species, including the recent H+ results. The accuracy, bias, and precision values are within the quality control standards listed in Table 3.

2.3.2 Ion Balance and Calculated Conductivity

Additional calculated parameters for evaluating laboratory quality are ion balance and calculated conductivity. A major objective of PCN is determination of the major ionic concentrations for all samples; once obtained, these results allow for a test of the validity of the measurements of the individual ions. The principle of electroneutrality dictates that the sum of all ionic charges in a solution be zero; thus, the sum of the anions should equal the sum of the cations (expressed in units of equivalents). The "ion balance" parameter IB (%) is defined as follows:

$$IB = \frac{S_A - S_C}{\left(\frac{S_A + S_C}{2}\right)} \times 100 \quad (5)$$

where S_A and S_C are the anion and cation sums ($\mu\text{eq/L}$), respectively. The quality assurance plan requires that reanalyses or other suitable corrective action be conducted if the absolute value of IB is greater than 20%. Frequently these actions do not lead to a change in the value of IB. This is likely due most often to the presence of ionic species (anions or cations) that are not measured by PCL, sometimes as a result of contamination by, or natural presence of, organic species. In the case of contamination, invalidation of the sample can often be justified on the basis of field notes or "reasonability" of the concentration values of one or more species. Thus, the ion balance test is not a certain indicator of analytical quality, but gives a strong indication of analytical or contamination problems.

A comparison of measured versus calculated conductivity offers another useful test of the accuracy of analytical measurements. Calculated conductivity (C_C) is the sum of the products of the individual ion's concentrations and specific conductivities:

$$\begin{aligned} C_C = & 0.35[H^+] + 0.2228[H^+]-1 + 0.0759[Cl^-] + 0.104[Ca^{2+}] \\ & + 0.0932[Mg^{2+}] + 0.0489[Na^+] + 0.0710[NO_3^-] + 0.1478[SO_4^{2-}] \\ & + 0.0745[NH_4^+] \end{aligned} \quad (6)$$

where the brackets denote molar concentrations. The conductivity test, or "conductivity balance" CB (%) is

$$CB = \frac{C_C - C_M}{C_M} \times 100, \quad (7)$$

where C_M is the measured conductivity. The criteria for reexamination of the analyses on the basis of CB depend on the value of measured conductivity:⁽¹⁴⁾

<u>If CB (%) is</u>	and	<u>C_M ($\mu\text{mho/cm}$) is</u>
>50		<5
>30		5 to 30
>20		>30

Tabulated statistics for IB and CB for 1985 and for the historical data record are listed in Section 3 (Table 11).

2.3.3 pH Measurement Bias

In the process of examining the ion balance statistics for 1985, an unusual trend toward positive IB values was detected (see Table 11). This trend was determined to be the result of a bias in pH measurements during the sample date period October 1985 through June 1986. Ninety-one samples from this period were reanalyzed for pH; comparisons of the "old" to the "new" values are shown in Figures 4 and 5. Statistics on the pH and H^+ differences are listed in Table 7. Since the pH of many samples will change during storage, it is not possible to determine the exact value of the bias. There is no doubt that some of the outlier measurements reflect these natural changes, but they can also counteract or enhance the appearance of the bias. The problem was determined to be a defective electrode; the normal quality control

FIGURE 4. Comparison of "Old" Versus "New" pH Measurement Data for Samples Dated October 1, 1985 to July 1, 1986. The solid line represents 1:1 correspondence.

FIGURE 5. Difference in H^+ (μM) Measurements Versus "New" Values for Samples from Bias Period

TABLE 7. pH Bias Statistics for Samples Dated Oct 1985 Through June 1986 (OLD) and Reanalyzed (NEW) Early in 1987

	NEW pH	OLD pH	pH DIFF	NEW H^+ (μM)	OLD H^+ (μM)	H^+ DIFF (μM)	H^+ DIFF %
All Samples (N = 91)							
MEAN	4.28	4.43	-0.15	76	59	18	23
STD DEV	0.43	0.54	0.46	73	52	49	
MEDIAN	4.24	4.37	-0.09	57	42	13	19
MINIMUM	3.37	3.47	-1.99	1	0	-111	-8610
MAXIMUM	5.97	6.77	1.94	427	339	391	99
Outliers Removed (N = 85)							
MEAN	4.26	4.35	-0.09	75	61	14	18
STD DEV	0.38	0.37	0.20	64	52	27	
MEDIAN	4.23	4.33	-0.09	59	47	12	19
MINIMUM	3.38	3.47	-0.76	2	1	-111	-641
MAXIMUM	5.69	5.85	0.87	417	339	151	83

procedures that would quickly identify the problem were compromised by improper training of pH analysts by network management. Data for this period have been flagged as uncertain in the ADS data base, and users are cautioned to ignore the apparent trend in pH and ion balance during the October 1985 to June 1986 period.

FIGURE 5. Difference in pH of Measurements Versus the Values for Samples from this Period

TABLE 2. pH Data Statistics for Samples from Oct 1985 through June 1986 (OLD) and Reanalyzed (NEW) Early in 1987

All Samples (N = 91)		NEW (N = 42)		OLD (N = 49)	
		Mean	Diff	Mean	Diff
MEAN	4.58	4.58	-0.12	4.58	0.00
STD DEV	0.43	0.43	0.00	0.43	0.00
MEDIAN	4.54	4.54	-0.03	4.54	0.00
MINIMUM	3.37	3.37	-1.00	3.37	0.00
MAXIMUM	5.97	5.97	1.00	5.97	0.00
Further Reanalyzed (N = 83)		NEW (N = 42)		OLD (N = 41)	
		Mean	Diff	Mean	Diff
MEAN	4.58	4.58	-0.09	4.58	0.00
STD DEV	0.38	0.38	0.00	0.38	0.00
MEDIAN	4.53	4.53	-0.05	4.53	0.00
MINIMUM	3.38	3.38	-0.15	3.38	0.00
MAXIMUM	5.89	5.89	0.00	5.89	0.00

3.0 DATA SUMMARY FOR 1985 AND 1977 THROUGH 1985

3.1 INTRODUCTION

The PCL data base, containing the PCN field observations and precipitation chemistry results, is regularly updated and subjected to the quality control measures described in Section 2 and in PCL quality control procedures (listed in Appendix A). Before statistical summaries can be generated, an editing process must be performed; this process, which is detailed in Appendix B, includes calculation of additional parameters and use of them to eliminate events that do not meet specified standards. These standards include considerations of: availability of precipitation amount data, missing or MDL species concentration data, and collection efficiency. The basic procedure used now is identical with that used in previous reports and publications, but additional calculated parameters have been added: ion balance, conductivity balance, and laboratory-field pH difference, which are used for quality evaluation and were described in Section 2; and sea-salt corrected sulfur, a parameter useful for evaluating the maritime influence at (particularly) the coastal sites.

The procedure used for calculating the sea-salt sulfur component of the precipitation sulfur is detailed in Appendix C. The procedure employs the sea-water ratios among Na, Cl, and Mg, and calculates the sea-salt contribution to sulfate on the basis of Na or Mg concentrations in the sample. If both Mg and Na are missing, the corrected value is taken as the original measured sulfur value. The procedure is that used in the ADS,⁽¹⁾ and is after Rahn.⁽¹⁵⁾ Because PCN measurements for Na and Mg were either missing or of dubious quality during 1977, summaries of sea-salt corrected sulfur (SSCS) begin with 1978.

The computer programs employed for statistical calculations all use the general editing procedure, but the program applications may vary in the specifications chosen in the editing process. For example, listings of editing statistics bypass the basic rejection criteria in order to display their effect, and treatment of the MDL values may vary. In addition, calculations that use more than one species (such as ion balance) apply the editing criteria to all species simultaneously; that is, the samples saved for the calculation

are only those that contain all the selected species. Thus, the ion balance and other multi-species statistics will in general apply to a smaller data set than concentration statistics for a single chemical species. Precipitation amount totals are computed both for all samples with precipitation amount entries, and for the samples surviving the edit for the selected chemical species. Precipitation amount also may be selected as a species. All calculations here are for whole-year or whole-month data sets (that is, sites are included in the given application data base beginning with the full month or year following the initiation of sampling).

The statistical results presented here are consistent in format and procedure with those presented in earlier periodic reports⁽⁸⁻¹²⁾ and in open-literature publications.^(2,3)

3.2 DISTRIBUTION STATISTICS

The "general statistics" programs determine basic statistical parameters for the unweighted species concentrations. Table 8 lists these parameters for major ionic species (species accounting for about 90% of the measured ionic equivalents) and precipitation amount for the 1985 data, and Table 9 similarly lists parameters for the 1977 through 1985 whole-years data base. The impact of the editing procedures on the data base is illustrated in Table 10, where editing statistics resulting from the application of the general statistics program to sulfur are presented. Because sulfur has the highest priority for chemical analysis, the numbers of samples rejected for insufficient sample volume will be the fewest among the species, and, because of the consistently above-MDL character of sulfur, the fewest MDL treatments appear. Otherwise, the editing statistics are quite similar among the species.

The concentrations and precipitation amount distributions are more closely described by log-normal than by normal distributions; this is suggested by better agreement between the geometric means and the medians, than between the arithmetic means and the medians.

General statistics for the quality control parameters ion balance, conductivity balance, lab-field pH difference, and collection efficiency are listed in Table 11 for 1985 only, and Table 12 for the period 1978 through

TABLE 8. MAP3S/PCN General Statistics for 1985

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Percentage of Samples					MAX
									5	25	MED	75	95	
S (μM)														
WH	140	116	1	29	30	20	2.3	2.2	5.2	11	20	38	78	243
IT	84	79	1	41	49	28	2.4	4.1	5.5	14	24	48	102	315
PS	101	85	1	42	33	31	2.3	2.6	7.4	17	33	56	103	158
VA	61	45	1	36	42	25	2.2	2.7	6.7	16	23	34	71	225
IL	97	63	1	38	30	29	2.1	3.6	9.5	19	30	48	73	196
BR	80	67	1	37	35	26	2.4	2.8	5.7	13	24	50	95	187
LE	54	45	1	32	22	25	2.1	4.3	7.0	16	30	40	75	92
OX	93	77	1	32	18	27	1.8	3.9	9.5	18	27	41	63	90
OR	64	63	1	37	24	30	1.9	6.2	9.8	18	31	49	83	116
SSCS (Sea-Salt Corrected $\text{SO}_4^{=}$) (μM)														
WH	140	116	1	29	30	20	2.4	2.2	4.9	11	19	37	78	240
IT	84	79	1	41	49	27	2.4	4.1	5.4	14	23	47	101	315
PS	101	85	1	42	33	31	2.3	2.4	7.2	17	33	55	103	157
VA	61	45	1	36	42	25	2.2	2.7	6.7	15	23	34	70	224
IL	97	63	1	37	30	29	2.1	3.6	9.5	19	29	47	73	196
BR	80	67	1	36	35	24	2.6	2.5	4.0	12	22	49	95	187
LE	54	45	1	28	23	20	2.5	2.2	3.3	11	25	35	74	91
OX	93	77	1	32	18	27	1.8	3.8	9.4	18	27	41	63	90
OR	64	63	1	37	24	30	1.9	5.9	8.1	18	30	48	82	116
NO_3 (μM)														
WH	140	116	1	37	30	26	2.4	2.7	6	15	28	47	105	135
IT	84	79	1	53	56	38	2.2	8.7	10	21	40	63	117	327
PS	101	85	1	47	31	39	1.9	8.2	14	23	41	57	104	191
VA	61	45	1	39	43	30	1.9	9.0	11	20	30	40	67	281
IL	97	63	1	41	35	31	2.0	7.4	10	16	31	41	120	175
BR	80	67	1	50	48	33	2.6	2.2	5	17	30	61	133	223
LE	54	45	1	33	30	22	2.7	2.5	3	13	23	37	91	125
OX	93	77	1	34	18	29	1.7	8.7	10	18	30	43	69	81
OR	64	63	1	30	18	25	1.8	8.6	9	15	27	38	59	99

TABLE 8. (contd)

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Percentage of Samples					MAX
									5	25	MED	75	95	
C1 (μM)														
WH	140	116	1	5.0	3.9	4.1	1.9	0.9	1.3	2.6	4.5	6.5	10	34
IT	84	79	1	10.3	17.8	6.2	2.5	1.4	1.7	3.0	5.7	11.5	23	140
PS	101	85	1	9.3	7.6	7.3	1.9	1.9	2.3	4.6	7.6	10.2	26	50
VA	61	45	1	9.1	7.4	7.2	2.0	1.6	2.2	4.5	7.2	9.6	18	41
IL	97	63	1	6.8	5.0	5.4	2.0	0.9	1.8	3.5	4.7	9.0	14	30
BR	80	67	1	27.9	33.5	18.3	2.4	3.1	4.8	10.2	15.7	26.2	90	178
LE	54	45	1	55.0	68.2	28.4	3.2	2.2	6.1	10.9	18.0	62.4	192	271
OX	93	77	1	6.8	4.7	5.5	2.0	1.1	1.6	3.2	5.3	8.6	14	23
OR	64	63	1	8.5	5.8	6.8	2.0	0.8	2.5	4.0	7.3	10.9	19	33
H (μM)														
WH	140	116	1	55	48	40	2.5	1.0	8.3	23	43	69	138	331
IT	84	79	1	77	80	53	2.5	2.5	10.5	32	53	85	191	447
PS	101	83	1	82	56	66	2.0	8.1	22.9	48	66	98	191	302
VA	61	45	1	61	54	49	1.9	10.5	13.5	30	47	66	110	331
IL	97	63	1	54	48	35	3.3	0.6	0.9	26	43	62	105	263
BR	80	66	1	73	61	45	3.4	0.3	2.5	29	55	105	170	309
LE	54	45	1	54	43	31	4.1	0.4	0.8	18	49	76	132	174
OX	93	77	1	55	27	49	1.6	9.5	20.0	35	49	65	98	158
OR	64	62	1	63	38	54	1.7	13.2	17.8	36	57	76	129	214
NH4 (μM)														
WH	140	115	1	21	27	12	3.2	*	1.5	5.1	14	23	72	164
IT	84	76	1	28	39	17	2.6	3.0	3.1	8.1	17	30	76	216
PS	101	79	1	24	24	16	2.6	2.1	2.4	8.0	18	27	81	115
VA	61	42	1	20	24	14	2.4	2.1	2.8	6.8	17	24	39	155
IL	97	63	1	32	32	22	2.5	2.1	4.8	13.1	23	40	83	151
BR	80	65	1	23	27	13	3.2	*	1.7	5.9	16	31	65	151
LE	54	45	1	21	18	12	3.2	0.6	1.0	5.2	17	29	58	64
OX	93	75	1	21	17	16	2.2	0.6	5.2	10.0	15	27	45	105
OR	64	63	1	16	13	11	2.8	*	1.0	5.6	12	20	40	54

TABLE 8. (contd)

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Percentage of Samples					MAX
									5	25	MED	75	95	
Na (μ M)														
WH	140	114	1	2.2	3.4	1.3	2.7	*	*	0.8	1.4	2.6	6	31
IT	84	75	1	3.2	4.2	1.7	3.3	*	*	0.7	2.0	3.2	11	26
PS	101	74	1	3.4	3.2	2.2	2.8	*	*	1.2	2.9	3.9	9	17
VA	61	42	1	4.5	4.4	2.8	2.8	*	*	1.4	2.4	6.0	11	17
IL	97	62	1	2.7	2.7	1.6	3.1	*	*	0.7	2.0	3.6	7	13
BR	80	63	1	25.9	34.7	14.7	2.8	0.9	3.3	7.6	13.2	25.3	82	183
LE	54	44	1	46.1	58.9	23.1	3.4	2.6	2.9	8.3	18.2	61.5	128	283
OX	93	70	1	3.2	3.2	2.1	2.6	*	*	1.2	2.1	4.3	9	16
OR	64	60	1	5.5	6.2	3.3	2.8	*	0.7	1.7	2.5	7.4	17	36

Precipitation (cm)

WH	140	133	1	0.93	1.28	0.45	3.6	0.0	0.04	0.19	0.49	1.0	3.3	7.8
IT	84	80	1	1.05	0.91	0.66	2.9	0.0	0.10	0.30	0.82	1.5	3.1	3.6
PS	101	92	1	1.08	1.26	0.46	5.0	0.0	0.02	0.19	0.59	1.5	3.3	5.7
VA	61	58	1	1.87	2.60	0.51	7.3	0.0	0.01	0.09	0.82	2.3	7.8	10.8
IL	97	78	1	1.29	1.75	0.36	9.2	0.0	0.00	0.13	0.53	1.7	4.2	8.6
BR	80	77	1	1.21	1.60	0.57	3.9	0.0	0.06	0.28	0.71	1.3	3.9	9.0
LE	54	53	1	2.18	3.32	1.00	3.8	0.1	0.06	0.45	1.09	2.5	5.9	20.9
OX	93	88	1	1.29	1.74	0.55	4.1	0.0	0.05	0.18	0.57	1.6	4.6	7.6
OR	64	63	1	1.79	1.96	1.03	3.2	0.1	0.10	0.44	1.20	2.4	6.0	10.6

LEGEND:

N	Total number of events
NEDT	Number of events after edit
YRS	Years in record analyzed
MIN	Minimum value
MAX	Maximum value
AME	Arithmetic mean
ASD	Arithmetic standard deviation
GME	Geometrical mean
GSD	Geometrical standard deviation
MED	Median (50th percentile)
*	At or below MDL

TABLE 9. MAP3S/PCN General Statistics for 1977 Through 1985

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Percentage of Samples					MAX
									5	25	MED	75	95	
S (μM)														
WH	859	739	9	28	25	20	2.3	1.3	4.9	11	22	36	77	243
IT	667	607	9	40	36	28	2.3	0.7	6.8	17	29	49	100	315
PS	831	715	9	44	38	32	2.4	1.9	6.6	18	36	58	110	340
VA	567	445	9	37	33	27	2.2	2.7	6.9	16	27	48	94	250
IL	685	433	8	40	30	32	1.9	2.5	11.4	21	32	51	87	280
BR	529	425	7	34	30	24	2.4	0.5	5.9	13	24	44	100	187
LE	480	398	7	30	24	23	2.1	1.9	6.7	14	22	40	70	160
OX	615	465	7	37	25	30	2.0	1.7	10.0	20	30	47	82	180
OR	322	313	5	37	29	29	1.9	4.3	9.4	19	30	45	84	250
SSCS (Sea-Salt Corrected $\text{SO}_4^{=}$) (μM)														
WH	859	739	9	28	25	20	2.3	1.3	4.7	11	22	36	77	240
IT	667	607	9	39	36	28	2.3	0.7	6.5	17	29	49	100	315
PS	831	715	9	44	37	31	2.4	1.8	6.3	18	35	58	110	340
VA	567	445	9	37	33	27	2.2	2.7	6.8	16	26	48	94	245
IL	685	433	8	40	29	32	1.9	2.4	11.1	21	32	50	86	280
BR	529	425	7	32	30	21	2.6	0.4	3.9	11	22	42	96	187
LE	480	398	7	27	24	18	2.5	0.7	3.6	10	19	37	67	157
OX	615	465	7	37	25	30	2.0	1.7	9.8	20	29	46	81	179
OR	322	313	5	36	29	29	1.9	4.1	8.9	19	30	45	83	250
NO_3 (μM)														
WH	859	740	9	32	28	23	2.3	*	5.8	13.0	24	41	86	260
IT	667	608	9	43	36	34	2.0	2.5	11.0	21.0	34	54	100	327
PS	831	715	9	50	38	39	2.1	2.0	11.0	25.0	41	63	130	280
VA	567	445	9	36	38	27	2.1	3.0	8.0	16.0	27	42	87	530
IL	685	433	8	40	29	32	1.9	6.5	11.0	19.9	32	49	100	175
BR	529	426	7	39	42	23	3.1	*	3.4	10.7	25	52	129	280
LE	480	398	7	31	32	19	2.8	*	2.9	9.2	21	41	90	320
OX	615	464	7	34	23	28	1.9	2.5	9.0	19.0	28	44	78	140
OR	322	313	5	28	21	22	2.0	1.8	6.5	14.0	23	35	70	130

TABLE 9. (contd)

SITE	N	NEOT	YRS	AME	ASO	GME	GSO	MIN	Percentage of Samples					MAX
									5	25	MEQ	75	95	
Cl (μM)														
WH	859	738	9	5.2	6.4	3.4	2.6	*	0.7	2.2	3.6	5.6	15	63
IT	667	608	9	7.5	9.3	5.1	2.5	*	1.4	3.1	5.1	8.7	20	140
PS	831	711	9	9.8	9.3	6.8	2.6	*	1.7	4.4	7.1	11.0	28	84
VA	567	437	9	11.6	27.3	6.7	2.5	*	1.7	3.9	6.3	11.0	30	460
IL	685	435	8	7.5	7.1	5.7	2.1	*	1.9	3.7	5.6	8.9	18	79
BR	529	427	7	37.4	47.3	23.2	2.6	1.6	4.8	12.0	21.3	45.0	110	540
LE	480	399	7	58.8	90.7	32.1	3.0	1.1	6.1	14.0	32.0	69.0	175	1200
OX	615	464	7	7.2	6.0	5.7	1.9	0.9	2.0	3.6	5.6	8.4	17	73
OR	322	313	5	8.4	6.8	6.7	1.9	0.8	2.5	4.1	6.4	11.0	20	51
H (μM)														
WH	859	727	9	58	44	44	2.2	0.5	12.3	27	48	76	135	372
IT	667	596	9	85	63	67	2.0	2.4	19.1	45	69	105	195	479
PS	831	669	9	92	65	70	2.4	0.2	17.0	49	78	115	229	479
VA	567	435	9	77	69	59	2.1	6.8	17.8	35	60	91	200	850
IL	685	451	8	62	55	40	3.3	0.3	1.6	31	49	78	159	603
BR	529	440	7	72	66	45	3.0	0.3	7.1	22	51	100	209	370
LE	480	400	7	58	51	39	2.7	0.4	7.1	21	45	81	150	331
OX	615	474	7	66	44	52	2.2	0.1	15.5	37	56	81	151	309
OR	322	312	5	65	49	52	1.9	1.6	17.8	35	53	81	151	398
NH4 (μM)														
WH	859	728	9	18	21	9.9	3.5	*	0.8	4.9	12	24	57	164
IT	667	604	9	23	24	13.8	3.0	*	2.0	7.4	16	30	61	216
PS	831	696	9	24	25	14.6	2.9	*	2.2	7.4	17	30	66	250
VA	567	440	9	20	22	11.8	3.1	*	1.5	6.1	14	26	55	200
IL	685	432	8	31	31	21.5	2.4	0.7	5.0	13.0	23	38	82	280
BR	529	426	7	19	24	9.6	3.7	*	0.9	4.1	11	25	61	160
LE	480	399	7	17	17	9.9	3.3	*	1.0	4.4	11	26	54	84
OX	615	462	7	23	21	15.8	2.7	*	2.7	9.8	17	30	59	200
OR	322	312	5	15	14	9.4	3.1	*	1.0	5.2	12	22	40	100

TABLE 9. (contd)

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Percentage of Samples					MAX	
									5	25	MED	75	95		
Na (μ M)															
WH	775	654	8	3.0	4.9	1.6	3.0	*	*	0.8	1.5	3.1	11	51	
IT	612	558	8	3.2	5.4	1.6	3.1	*	*	0.7	1.6	3.1	13	66	
PS	737	616	8	5.2	6.7	2.8	3.2	*	*	1.4	2.9	5.8	20	47	
VA	516	393	8	7.5	23.1	3.1	3.3	*	0.5	1.3	2.9	6.3	22	390	
IL	685	432	8	4.5	6.5	2.5	2.9	*	0.4	1.3	2.5	4.8	15	78	
BR	529	423	7	32.4	41.5	18.3	3.1	0.4	2.9	8.5	19.0	41.0	100	450	
LE	480	397	7	49.7	70.7	25.3	3.5	0.4	2.6	11.0	26.1	63.0	160	890	
OX	615	456	7	4.4	5.0	2.7	2.8	*	0.5	1.3	2.6	5.3	14	34	
OR	322	308	5	6.3	8.8	3.4	3.0	*	0.6	1.6	3.4	7.1	21	57	
Precipitation (cm)															
WH	859	830	9	1.20	1.41	0.64	3.6	0.0	0.06	0.29	0.76	1.6	3.8	12.9	
IT	667	629	9	1.43	1.45	0.84	3.2	0.0	0.09	0.42	0.97	1.9	4.5	9.2	
PS	831	792	9	1.22	1.47	0.53	4.6	0.0	0.03	0.20	0.70	1.7	4.4	10.6	
VA	567	502	9	1.79	2.18	0.81	4.3	0.0	0.05	0.33	0.97	2.3	5.7	14.5	
IL	685	601	8	1.02	1.46	0.30	7.4	0.0	0.01	0.09	0.46	1.4	3.7	12.7	
BR	529	494	7	1.61	1.86	0.80	3.8	0.0	0.08	0.31	0.87	2.3	5.1	12.1	
LE	480	460	7	1.66	2.08	0.78	4.2	0.0	0.05	0.33	0.96	2.3	5.1	20.9	
OX	615	579	7	1.18	1.45	0.54	4.2	0.0	0.03	0.20	0.68	1.7	4.2	11.1	
OR	322	318	5	1.97	2.04	1.14	3.2	0.0	0.13	0.48	1.33	2.6	6.2	14.6	

LEGEND:

N	Total number of events
NEDT	Number of events after edit
YRS	Years in record analyzed
MIN	Minimum value
MAX	Maximum value
AME	Arithmetic mean
ASD	Arithmetic standard deviation
GME	Geometrical mean
GSD	Geometrical standard deviation
MED	Median (50th percentile)
*	At or below MDL

TABLE 10. Editing Statistics for Sulfur Distribution Statistics

SITE	N	NEDT	YRS	Numbers of Events							PFR
				VOL	CE	MDL	ISA	NAP	MOE	RPC	
1985											
WH	140	116	1	6	1	0	15	0	2	0	0.997
IT	84	79	1	0	4	0	1	0	0	0	0.965
PS	101	85	1	3	6	0	7	0	0	0	0.990
VA	61	45	1	1	2	0	13	0	0	0	0.996
IL	97	63	1	4	15	0	15	0	0	0	0.916
BR	80	67	1	0	3	0	10	0	0	0	0.992
LE	54	45	1	0	1	0	8	0	0	0	1.000
OX	93	77	1	1	4	0	11	0	0	0	0.995
OR	64	63	1	0	1	0	0	0	0	0	0.965
1977-1985											
WH	859	739	9	12	17	0	72	2	11	6	0.982
IT	667	607	9	3	35	0	14	2	3	3	0.955
PS	831	715	9	15	24	0	67	0	5	5	0.981
VA	567	445	9	17	48	0	51	0	4	2	0.920
IL	685	433	8	9	75	0	151	3	11	3	0.853
BR	529	425	7	4	31	0	59	0	3	7	0.966
LE	480	398	7	2	18	0	61	0	1	0	0.923
OX	615	464	7	2	34	1	105	0	5	4	0.962
OR	322	313	5	0	4	0	2	0	0	3	0.977

LEGEND:

N	Total number of events
NEDT	Number of events after edit
YRS	Years in record analyzed
VOL	Precipitation missing
CE	Collection efficiency below 0.5
MDL	Species concentration below mdl
ISA	Insufficient sample for analysis
NAP	No analysis performed
MOE	Malfunction or operator error
RPC	Probable contamination
PFR	Fraction of precipitation in remaining events

TABLE 11. General Statistics for QC Parameters -- 1985

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centile Values					MAX
									5	25	MED	75	95	
Ion Balance (%)														
WH	140	112	1	15	24	11	3.7	-69	-15	0	14	23	62	107
IT	84	70	1	17	20	13	3.5	-42	-15	4	15	26	44	97
PS	101	67	1	10	19	12	2.5	-34	-22	-6	11	20	38	67
VA	61	40	1	20	17	15	2.7	-11	-6	5	19	30	46	72
IL	97	61	1	8	16	8	3.6	-38	-21	-4	8	17	30	55
BR	80	61	1	6	20	8	3.6	-49	-29	-6	5	15	41	67
LE	54	44	1	6	25	13	2.7	-58	-58	-10	7	19	41	71
OX	93	69	1	11	16	11	2.3	-30	-17	2	11	18	35	59
OR	64	59	1	13	20	13	2.9	-60	-32	1	16	24	38	72
Conductivity Balance (%)														
WH	140	112	1	-13	23	10	3.3	-68	-57	-21	-13	-2	6	157
IT	84	70	1	-12	16	10	4.0	-45	-38	-26	-13	0	8	28
PS	101	67	1	-9	12	6	4.3	-40	-27	-19	-7	0	6	16
VA	61	40	1	-14	16	9	4.7	-51	-41	-24	-13	0	5	13
IL	97	61	1	-8	14	7	3.1	-73	-29	-15	-5	2	6	11
BR	80	61	1	-7	28	9	3.5	-62	-47	-18	-10	3	8	166
LE	54	44	1	-12	14	10	3.7	-41	-40	-22	-12	-3	11	17
OX	93	69	1	2	84	8	4.0	-43	-33	-17	-8	-1	9	669
OR	64	59	1	-11	15	10	2.7	-39	-36	-20	-10	-2	10	48
pH Difference														
WH	140	112	1	0.09	0.19	0.10	2.5	-0.4	-0.1	0.0	0.08	0.19	0.32	1.3
IT	84	70	1	0.14	0.14	0.11	2.5	-0.0	-0.0	0.1	0.12	0.19	0.29	0.9
PS	101	67	1	0.13	0.13	0.09	2.9	-0.1	-0.0	0.0	0.10	0.21	0.35	0.6
VA	61	40	1	0.17	0.16	0.11	3.2	-0.0	-0.0	0.1	0.13	0.25	0.43	0.7
IL	97	61	1	0.03	0.16	0.07	2.7	-0.6	-0.4	0.0	0.04	0.13	0.20	0.3
BR	80	61	1	0.14	0.30	0.08	3.3	-0.4	-0.0	0.0	0.08	0.15	0.30	1.7
LE	54	44	1	0.14	0.21	0.12	2.6	-0.2	-0.2	0.1	0.12	0.20	0.34	0.9
OX	93	69	1	0.12	0.11	0.10	2.4	-0.0	-0.0	0.0	0.11	0.17	0.30	0.5
OR	64	59	1	0.06	0.16	0.09	2.5	-0.2	-0.2	-0.1	0.04	0.12	0.39	0.5
Collection Efficiency														
WH	140	131	1	1.11	0.24	1.09	1.2	0.60	0.82	0.99	1.08	1.17	1.56	2.4
IT	84	80	1	0.90	0.14	0.89	1.2	0.50	0.61	0.84	0.94	1.00	1.06	1.2
PS	101	88	1	1.07	0.20	1.06	1.2	0.59	0.74	1.00	1.04	1.15	1.41	1.7
VA	61	56	1	1.13	0.35	1.09	1.2	0.61	0.68	0.99	1.04	1.12	1.85	2.7
IL	97	67	1	0.91	0.20	0.89	1.2	0.52	0.52	0.77	0.94	0.99	1.16	1.6
BR	80	75	1	1.14	0.56	1.07	1.4	0.57	0.63	0.93	1.02	1.11	2.20	4.2
LE	54	49	1	1.06	0.24	1.04	1.2	0.56	0.70	0.96	1.07	1.12	1.28	2.3
OX	93	86	1	1.04	0.33	1.00	1.2	0.51	0.62	0.92	1.03	1.11	1.25	3.5
OR	64	60	1	1.19	0.55	1.13	1.3	0.61	0.84	1.04	1.10	1.19	1.66	5.1

TABLE 12. General Statistic for QC Parameters -- 1978 Through 1985

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centile Values					
									5	25	MED	75	95	MAX
Ion Balance (%)														
WH	775	627	8	4.1	20	7.8	3.4	-93	-24	-4.7	3.5	12.7	33	107
IT	612	529	8	3.5	15	7.1	3.3	-65	-19	-4.8	3.5	11.1	26	97
PS	737	543	8	2.3	16	8.4	2.7	-68	-21	-6.9	3.2	10.8	25	67
VA	516	368	8	2.6	16	7.2	3.2	-50	-24	-6.3	1.6	10.5	30	72
IL	685	393	8	2.9	15	7.6	3.3	-59	-25	-5.2	3.8	11.0	27	78
BR	529	411	7	3.1	15	6.7	3.1	-55	-17	-5.1	2.0	10.0	25	108
LE	480	384	7	1.1	15	6.5	3.2	-63	-22	-6.6	1.5	8.3	22	71
OX	615	438	7	3.7	14	7.0	2.9	-78	-17	-4.2	3.8	10.1	25	75
OR	322	304	5	6.6	14	7.3	3.2	-60	-16	-0.8	6.2	14.2	29	72
Conductivity Balance (%)														
WH	775	627	8	-3.0	15.0	5.8	3.3	-68	-22	-9.7	-2.4	3.7	17.9	157
IT	612	529	8	0.3	42.7	5.3	3.7	-75	-22	-7.8	-0.9	4.9	19.6	936
PS	737	543	8	-1.7	12.5	5.7	3.3	-58	-21	-8.2	-2.2	4.6	18.6	67
VA	516	368	8	-1.7	12.8	5.8	3.2	-51	-23	-7.9	-1.5	5.9	14.6	67
IL	685	393	8	-3.6	11.4	5.1	3.4	-73	-21	-11	-3.4	2.2	12.0	47
BR	529	411	7	-1.1	23.6	5.5	3.6	-62	-21	-9.9	-1.4	4.5	18.4	352
LE	480	384	7	-0.5	12.3	5.6	3.1	-69	-20	-7.9	-0.9	6.0	18.7	56
OX	615	438	7	-0.2	35.3	5.9	3.1	-43	-18	-8.8	-3.9	3.4	18.2	669
OR	322	304	5	-4.5	9.4	4.5	3.3	-39	-21	-8.8	-4.0	0.3	9.4	48
pH Difference														
WH	775	627	8	0.12	0.21	0.11	2.8	-0.5	-0.1	0.0	0.09	0.23	0.47	1.3
IT	612	529	8	0.03	0.10	0.05	2.4	-0.9	-0.1	0.0	0.03	0.07	0.18	0.9
PS	737	543	8	0.00	0.29	0.08	3.0	-2.9	-0.3	-0.1	0.0	0.05	0.27	2.3
VA	516	368	8	0.07	0.14	0.07	2.7	-0.4	-0.1	0.0	0.06	0.12	0.28	0.9
IL	685	393	8	0.03	0.18	0.07	2.9	-0.7	-0.2	0.0	0.03	0.08	0.24	1.4
BR	529	411	7	0.12	0.26	0.08	2.9	-1.4	-0.1	0.0	0.08	0.15	0.44	2.0
LE	480	384	7	0.07	0.18	0.08	2.7	-0.9	-0.2	0.0	0.06	0.13	0.30	1.1
OX	615	438	7	0.13	0.34	0.16	3.0	-2.6	-0.4	0.0	0.11	0.27	0.62	1.8
OR	322	304	5	0.05	0.12	0.06	2.6	-0.4	-0.1	0.0	0.04	0.10	0.26	0.7
Collection Efficiency (1977-1985)														
WH	859	804	9	1.19	0.49	1.13	1.3	0.50	0.75	1.00	1.10	1.25	1.78	8.7
IT	667	617	9	0.93	0.16	0.92	1.2	0.50	0.62	0.88	0.96	1.01	1.13	2.0
PS	831	700	9	1.11	0.37	1.07	1.3	0.50	0.68	0.94	1.04	1.19	1.76	4.6
VA	567	454	9	1.13	0.39	1.08	1.3	0.51	0.76	0.96	1.04	1.16	1.80	5.2
IL	685	498	8	1.01	0.36	0.97	1.3	0.50	0.58	0.87	0.98	1.04	1.51	4.7
BR	529	484	7	1.12	0.80	1.04	1.3	0.51	0.66	0.93	1.03	1.10	1.54	13
LE	480	430	7	1.30	5.05	1.03	1.4	0.52	0.64	0.90	1.01	1.12	1.60	106
OX	615	541	7	1.06	0.50	1.01	1.3	0.50	0.63	0.91	1.00	1.09	1.55	8.4
OR	322	313	5	1.12	0.28	1.10	1.1	0.61	0.91	1.03	1.09	1.14	1.34	5.1

1985 (because data were inadequate for important species in the 1977 samples, that year was not included in the application data base). These variables were defined and discussed in Section 2.

3.3 WEIGHTED AVERAGES

Monthly and annual averages, weighted by precipitation amount, were calculated as follows:

$$C = \frac{\sum_{i=1}^n c_i p_i}{\sum_{i=1}^n p_i} \quad (8)$$

where c_i and p_i are concentration and precipitation amount, respectively, of the i th event; n is the number of events in the period (month or year); and C is the weighted average. This average is, in principle, the concentration that would be obtained if a single sample was collected over the full period. In practice, of course, such a sample would probably show a different value due to chemical changes associated with long exposure to field conditions and reactions caused by mixing of individual events, which generally vary in chemical characteristics.

Table 13 is a list of 1985 monthly weighted averages for the four major ionic species [S (assumed as $SO_4^{=}$), NO_3^- , H^+ , NH_4^+], precipitation per event, and precipitation total per month. A few of the site/months show blank entries: these result from situations where the number of samples removed by the editing process was sufficient to result in less than 50% of the precipitation during the month being represented by the average.

The entire data record for each site (up to 9 years) is summarized by considering the composite of all the available years for each month, or the "accumulated" monthly weighted averages (AMWA). The AMWA provides a description of the seasonal trends in species concentrations which is smoothed in terms of year-to-year variations (primarily due to precipitation amount variability). These are listed in Table 14, where added to the previously listed species is percent sea-salt sulfur.

TABLE 13. Monthly Weighted Averages for 1985

SITE	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YEAR
S (μM)													
WH		13	16	28	41	18	34	41	8	23	9	9	21
IT	14	25	18	36	41	37	45	69	24	28	14	15	29
PS		9	23	30	35	59	49	47	36	36	17	15	31
VA	12	23	21	27	22	47	37	25	11	17	14	12	24
IL	17	19	33	23	28			32	28	33	18	14	26
BR	13	14	38	31	27	33	40	20	45	17	11	21	24
LE		18	17	39	21	55	43	16	18	15	22	18	22
OX	11	20	28	31	37	26	42	30	26	17	19	14	26
OR	23	23	39	17		31	40	25	30	19	20	15	28
NO ₃ (μM)													
WH		23	29	38	32	18	20	24	6	21	17	31	23
IT	48	57	27	40	39	36	51	40	20	28	19	47	35
PS		30	28	36	29	50	39	35	33	33	23	33	33
VA	27	20	37	31	23	41	25	16	17	17	19	22	23
IL	11	16	29	27	26			21	26	31	16	21	23
BR	38	15	48	47	26	30	33	17	36	18	14	62	27
LE		15	14	52	21	65	26	13	7	15	13	27	19
OX	28	22	22	36	31	20	31	23	17	17	18	24	24
OR	23	21	28	13		26	24	16	18	13	19	14	20
H (μM)													
WH		47	47	36	60	37	56	75	29	29	15	35	42
IT	57	96	46	49	63	50	91	110	30	50	31	52	56
PS		40	59	68	69	99	88	84	61	60	44	50	65
VA	38	46	68	36	36	48	65	47	19	29	45	33	44
IL	32	43	61	37	52			52	34	42	26	33	43
BR	58	29	78	58	47	77	58	33	77	30	27	77	49
LE		39	38	60	29	106	62	27	14	18	23	38	36
OX	40	59	56	59	63	47	75	47	34	33	35	39	49
OR	69	60	75	27		33	61	52	46	36	45	32	50

TABLE 13. (contd)

<u>SITE</u>	<u>JAN</u>	<u>FEB</u>	<u>MAR</u>	<u>APR</u>	<u>MAY</u>	<u>JUN</u>	<u>JUL</u>	<u>AUG</u>	<u>SEP</u>	<u>OCT</u>	<u>NOV</u>	<u>DEC</u>	<u>YEAR</u>
NH₄ (μM)													
WH		5	13	39	29	11	25	13	3	15	5	6	13
IT	15	11	16	47	33	23	20	25	16	24	5	11	19
PS		5	16	21	22	46	29	19	18	26	7	7	19
VA	4	10	14	26	16	37	16	10	6	11	5	8	13
IL	7	13	28	23	20			15	21	53	11	8	18
BR	9	5	25	27	18	21	10	21	27	14	4	11	15
LE		5	6	37	21	41	22	8	6	7	5	9	12
OX	7	13	18	25	28	12	23	12	14	13	10	7	16
OR	11	5	24	9		17	16	12	9	3	6	5	12

Precipitation/Event (cm)

WH	0.54	0.92	0.79	0.54	0.95	0.81	0.63	0.98	2.13	1.15	1.28	0.63	0.93
IT	0.71	0.96	1.19	0.74	0.80	0.96	1.07	1.05	1.17	0.94	1.91	0.79	1.03
PS	0.40	0.94	1.48	0.74	1.48	0.97	0.89	0.94	1.90	0.50	2.08	0.50	1.02
VA	1.88	2.85	0.83	0.58	2.33	0.76	2.31	2.28	0.57	3.36	1.98	2.17	1.81
IL	0.80	1.62	1.36	1.33	0.89	0.58	1.03	1.42	0.74	0.67	2.38	0.77	1.18
BR	0.60	1.45	0.86	0.53	1.32	1.48	0.85	2.16	0.68	0.98	2.56	0.40	1.18
LE	1.56	2.19	1.05	0.60	1.92	0.85	2.43	5.53	3.22	1.44	1.12	2.36	2.14
OX	0.51	1.34	1.56	0.89	1.38	1.28	0.84	1.24	0.58	1.54	2.53	0.84	1.24
OR	1.05	2.37	0.95	1.73	1.32	1.37	2.13	3.50	1.32	2.29	2.07	2.21	1.83

Precipitation/Period (cm)

WH	5.4	9.2	8.7	8.0	13.3	13.0	5.0	11.7	19.2	10.3	15.4	5.0	124
IT	4.3	4.8	9.5	5.9	4.8	8.6	7.5	5.3	7.0	6.6	15.3	7.1	87
PS	3.2	4.7	11.8	7.4	8.9	10.6	8.0	7.5	7.6	4.0	20.8	5.5	100
VA	5.6	11.4	3.3	2.9	16.3	6.8	16.2	18.3	1.7	13.4	4.0	8.7	109
IL	5.6	9.7	9.5	10.6	7.1	5.8	9.3	12.8	1.5	5.4	26.2	6.2	110
BR	3.0	5.8	6.9	4.2	13.2	14.8	6.0	13.0	2.7	3.9	17.9	2.8	94
LE	6.2	8.8	5.3	2.4	9.6	6.0	9.7	38.7	12.9	4.3	4.5	7.1	115
OX	3.5	6.7	12.5	8.9	13.8	12.8	7.6	9.9	1.7	10.8	20.2	5.9	114
OR	6.3	11.9	5.7	6.9	9.2	9.6	19.1	21.0	5.3	6.9	6.2	8.8	117

TABLE 14. Monthly Weighted Averages Accumulated Over
All Available Years, 1977 Through 1985

SITE	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YEAR
S (μM)													
WH	9	13	16	24	27	32	26	36	20	19	12	10	22
IT	11	17	18	29	33	45	48	52	33	24	17	13	30
PS	12	17	23	33	36	46	55	57	39	24	17	17	32
VA	12	16	18	26	29	37	35	44	29	19	20	15	26
IL	22	23	29	31	28	37	40	36	35	26	21	19	30
BR	14	15	21	18	28	23	36	32	37	18	12	16	22
LE	14	18	21	23	29	37	37	27	28	21	17	16	24
OX	16	25	29	31	33	35	47	51	26	25	20	18	30
OR	25	22	25	21	27	35	37	34	32	21	21	16	26
NO ₃ (μM)													
WH	28	27	24	26	23	24	18	22	15	19	18	21	21
IT	28	39	29	32	31	33	30	31	27	26	22	27	29
PS	27	30	30	35	33	33	36	36	33	27	22	28	31
VA	16	20	20	24	25	27	25	28	20	19	25	18	23
IL	24	25	28	30	25	29	29	26	26	22	19	21	25
BR	11	14	19	16	26	19	32	30	32	18	12	17	20
LE	17	17	15	19	23	31	29	18	20	17	16	16	20
OX	19	27	29	28	22	26	31	32	21	21	18	17	24
OR	18	15	17	15	20	26	25	22	21	13	16	12	18
H (μM)													
WH	38	45	43	48	46	60	49	71	41	41	33	35	46
IT	41	59	48	66	69	86	97	99	70	57	46	43	67
PS	42	51	57	72	67	91	106	114	76	57	45	52	70
VA	41	42	43	52	56	74	65	87	56	42	55	42	56
IL	46	52	55	44	43	55	70	60	54	42	33	45	51
BR	25	30	43	34	47	47	71	78	73	36	27	37	44
LE	33	35	33	38	47	66	72	53	49	34	39	34	44
OX	44	57	57	54	47	57	92	92	47	52	41	42	57
OR	50	45	45	36	37	60	63	67	57	42	45	39	48

TABLE 14. (contd)

SITE	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YEAR
NH₄ (μM)													
WH	8	7	10	16	19	19	15	17	12	10	8	8	13
IT	8	8	11	18	19	25	20	23	16	15	9	9	16
PS	6	9	14	18	24	22	29	23	21	13	8	8	17
VA	4	7	9	16	19	21	16	20	16	10	9	6	13
IL	11	12	21	26	20	23	23	20	26	22	18	10	20
BR	3	5	10	9	20	13	20	17	18	10	5	6	11
LE	5	7	9	14	18	21	20	14	14	12	7	6	12
OX	6	14	21	23	23	22	22	24	15	16	11	11	18
OR	7	5	12	10	23	18	14	13	15	7	7	5	11

Precipitation/Event (cm)

WH	0.77	0.96	0.93	1.07	1.26	1.07	1.06	1.31	1.55	1.61	1.45	1.25	1.20
IT	1.36	1.34	1.41	1.36	1.35	1.49	1.44	1.39	1.75	1.47	1.51	1.15	1.42
PS	0.95	1.10	1.28	1.14	1.63	1.34	1.24	1.30	1.28	1.20	1.30	0.83	1.21
VA	1.88	1.99	1.69	1.99	1.91	1.35	1.72	1.67	1.80	1.89	2.02	1.60	1.78
IL	0.57	0.80	0.85	0.90	1.19	0.92	1.49	1.96	0.78	0.93	1.24	0.85	1.06
BR	1.94	1.83	1.44	1.96	1.22	1.86	1.20	1.40	1.38	1.54	1.87	1.33	1.57
LE	1.45	1.29	2.27	1.96	2.19	1.63	1.36	2.16	1.88	1.73	1.83	1.30	1.75
OX	0.62	1.07	1.11	1.14	1.45	1.05	1.25	1.06	0.82	1.31	1.78	1.14	1.17
OR	1.56	2.32	1.79	2.05	2.14	1.41	1.71	1.89	2.01	2.34	2.58	2.41	1.99

Precipitation/Period (cm)

WH	4.7	5.6	7.5	10.0	9.6	9.7	8.3	12.6	13.1	11.3	10.7	9.6	113
IT	8.0	6.4	8.6	8.9	7.2	10.6	8.5	9.9	9.9	9.3	9.5	7.7	105
PS	7.2	7.2	9.5	8.6	11.2	12.5	9.4	9.9	7.8	8.8	10.0	7.5	110
VA	7.7	9.3	9.4	9.9	10.2	6.7	11.8	11.9	7.4	9.2	7.4	7.7	109
IL	2.4	3.6	7.1	7.3	8.0	6.9	10.1	12.8	4.0	5.3	7.9	5.2	81
BR	7.8	7.5	9.6	11.3	7.5	11.4	6.4	7.8	5.8	7.6	10.2	7.5	100
LE	6.4	6.9	11.3	8.9	9.5	8.5	7.7	13.2	7.1	8.1	7.7	6.2	102
OX	3.0	4.8	6.5	7.5	10.8	6.5	8.1	6.1	3.6	7.6	9.9	7.2	82
OR	4.3	6.4	5.4	5.9	7.6	5.2	6.5	6.5	4.0	6.0	6.3	7.0	71

S/NO₃ (Molar) (Ratio of Averages)

WH	0.33	0.49	0.63	0.94	1.21	1.35	1.45	1.65	1.36	1.02	0.71	0.49	1.03
IT	0.40	0.44	0.63	0.90	1.07	1.38	1.57	1.66	1.26	0.91	0.74	0.48	1.01
PS	0.45	0.58	0.77	0.95	1.08	1.40	1.56	1.59	1.18	0.91	0.76	0.63	1.05
VA	0.73	0.80	0.91	1.06	1.14	1.39	1.41	1.59	1.44	1.00	0.80	0.81	1.16
IL	0.91	0.93	1.02	1.03	1.14	1.27	1.38	1.36	1.36	1.15	1.13	0.87	1.17
BR	1.21	1.10	1.12	1.18	1.08	1.17	1.13	1.07	1.17	1.04	1.04	0.93	1.11
LE	0.85	1.06	1.38	1.19	1.27	1.18	1.28	1.49	1.44	1.24	1.01	1.02	1.24
OX	0.85	0.96	0.99	1.11	1.49	1.32	1.52	1.57	1.19	1.22	1.16	1.06	1.25
OR	1.41	1.48	1.48	1.39	1.32	1.37	1.48	1.58	1.58	1.65	1.37	1.35	1.45

TABLE 14. (contd)

<u>SITE</u>	<u>JAN</u>	<u>FEB</u>	<u>MAR</u>	<u>APR</u>	<u>MAY</u>	<u>JUN</u>	<u>JUL</u>	<u>AUG</u>	<u>SEP</u>	<u>OCT</u>	<u>NOV</u>	<u>DEC</u>	<u>YEAR</u>
Sea-Salt S (%)													
WH	1.3	2.0	1.0	0.7	0.7	0.5	0.5	0.3	0.5	0.8	0.9	0.9	0.6
IT	1.7	1.9	1.4	0.6	0.4	0.5	0.5	0.2	0.4	0.6	0.9	1.5	0.6
PS	2.0	2.2	1.2	0.8	0.5	0.4	0.4	0.5	0.7	0.8	1.6	1.3	0.8
VA	3.5	4.6	2.3	1.7	0.9	0.4	0.7	0.5	1.1	1.9	2.9	2.3	1.4
IL	1.2	1.1	0.9	0.8	0.4	0.6	0.6	0.6	0.6	0.6	1.1	1.2	0.7
BR	14.4	16.5	13.4	10.0	4.8	2.7	2.2	2.4	4.5	13.2	16.5	16.6	8.1
LE	18.4	33.9	30.2	16.2	10.0	5.4	2.9	2.1	15.5	23.8	25.6	24.2	14.3
OX	1.8	1.2	1.0	0.8	0.6	0.6	0.4	0.5	0.6	0.5	1.1	1.2	0.7
OR	1.3	1.2	1.2	2.0	1.6	1.0	0.5	0.7	0.8	1.1	1.9	1.7	1.2

(Sea-Salt Corrected S)/NO₃ (Ratio of Averages)

WH	0.32	0.48	0.63	0.93	1.20	1.35	1.44	1.65	1.36	1.01	0.70	0.48	1.02
IT	0.40	0.43	0.62	0.90	1.07	1.37	1.57	1.65	1.26	0.91	0.73	0.48	1.01
PS	0.44	0.57	0.76	0.94	1.08	1.39	1.55	1.59	1.17	0.90	0.74	0.62	1.04
VA	0.70	0.77	0.89	1.05	1.13	1.39	1.40	1.58	1.42	0.98	0.78	0.80	1.14
IL	0.90	0.92	1.01	1.02	1.14	1.26	1.37	1.35	1.35	1.15	1.11	0.86	1.16
BR	1.03	0.92	0.97	1.06	1.03	1.14	1.10	1.04	1.12	0.90	0.87	0.78	1.02
LE	0.69	0.70	0.96	1.00	1.14	1.11	1.25	1.46	1.22	0.94	0.75	0.77	1.06
OX	0.84	0.94	0.98	1.10	1.48	1.31	1.51	1.56	1.19	1.21	1.14	1.05	1.24
OR	1.39	1.46	1.46	1.36	1.30	1.36	1.47	1.57	1.57	1.63	1.34	1.33	1.43

(Sea-Salt Corrected S)/NO₃ (Average of Ratio)

WH	0.53	0.69	0.75	1.07	1.26	1.40	1.47	1.75	1.52	1.12	0.84	0.60	1.16
IT	0.53	0.56	0.69	0.95	1.12	1.40	1.65	1.76	1.34	0.99	0.88	0.54	1.08
PS	0.57	0.69	0.87	1.00	1.14	1.42	1.58	1.65	1.24	1.01	0.87	0.83	1.10
VA	0.92	0.94	1.01	1.11	1.12	1.48	1.38	1.62	1.50	0.93	0.91	0.92	1.18
IL	1.30	1.04	1.17	1.07	1.16	1.33	1.41	1.44	1.47	1.24	1.21	1.03	1.25
BR	1.66	1.18	1.29	1.45	1.14	2.23	1.09	1.19	1.23	1.09	1.10	1.12	1.35
LE	1.00	1.22	1.14	1.47	1.17	1.16	2.16	1.64	1.19	1.39	1.02	1.14	1.33
OX	1.23	1.13	1.11	1.27	1.59	1.39	1.59	1.61	1.36	1.21	1.36	1.27	1.37
OR	2.06	1.95	1.61	1.38	1.36	1.38	1.39	1.61	1.61	1.70	1.56	1.80	1.61

Not surprisingly, the Brookhaven and Lewes sites show significant marine-origin sulfate. The sea-salt contribution to monthly average sulfur can be significant during the cooler months, as seen in Figure 6; this seasonal pattern is probably due to the increased incidence of frontal storms related to Atlantic low-pressure areas. These storms produce onshore transport and frequently large precipitation amounts during the winter months. The same seasonal pattern is seen for most of the other sites, but the magnitudes of the sea-salt contribution are much smaller.

The ratio of sulfur (assumed as sulfate) to nitrate illustrates the relative contributions to wet deposition of the two main anions. In considering weighted averages, however, the method of calculation will affect the results, as will whether one uses sulfur or SSCS for the numerator. Ratio averages can be computed several ways: as a ratio of the weighted averages of the species (Method A), as a weighted average of the ratios (Method B), or as the antilogarithm of a weighted average of the logarithms of the ratios (Method C). Method A would seem to be appropriate for expressing the ratio of deposition

FIGURE 6. Accumulated Monthly Weighted Average (AMWA) Percent SSCS for Brookhaven and Lewes Sites: 1977 Through 1985 Data Base

over a time period, since the true deposited masses of each species are compared. Method B is more applicable for analyzing the effect of scavenging mechanisms that vary from event to event for each species; that is, the variable relationship between the concentrations of the two species and precipitation amount is taken into account. In the case of nitrate and sulfur, although the concentrations of both species decrease with increasing precipitation amount, the decrease for nitrate is greater.⁽³⁾ [It should be kept in mind, however, that the correlations for the relationships are not strong.⁽³⁾] Therefore, large precipitation events will have higher ratios, and the Method B weighted average will be higher in general than those of Method A. Method C is an extension of Method B, in that the logarithms are used to attempt to account for the relationships among species concentrations and precipitation amounts that are generally distributed lognormally. Method C should tend to reduce the effect of outlier event ratios on the average.

Table 15 is a list of the 9-year AMWA for the ratios, calculated by the various methods, with both sulfur and SSCS used as numerator. The SSCS ratios are always smaller than the sulfur-based ratios for each method, with only the coastal sites showing a significant difference. The Method B ratios are higher than those for Method A, by varying amounts temporally and spatially, and Method C falls in between. Figures 7 and 8 compare the three methods for SSCS for Brookhaven and Lewes. Some outlier ratio values occur during the summer months, affecting Method B; otherwise, the differences between the methods generally are only significant during the cooler months (true for the other sites as well, but the magnitudes of the differences are much less). Figures 9 and 10 compare the sulfur with the SSCS-based ratios for Brookhaven and Lewes, using Method C. The primary sea-salt influence, as noted above, occurs during the cooler months.

The AMWA were illustrated by Dana and Easter⁽³⁾ for five years of data (1979-1983). The seasonal trends in most cases are not different for the present larger data set (except that the newer sites' results are smoothed somewhat due to larger data bases); the ratios presented, however, were for uncorrected sulfur and Method A only. The SSCS and Method B calculations on the earlier data base do not show significantly different seasonal trends than those with the present data.

TABLE 15. Sulfur/Nitrate Ratio (Molar); See Text for Description of Methods

<u>SITE</u>	<u>JAN</u>	<u>FEB</u>	<u>MAR</u>	<u>APR</u>	<u>MAY</u>	<u>JUN</u>	<u>JUL</u>	<u>AUG</u>	<u>SEP</u>	<u>OCT</u>	<u>NOV</u>	<u>DEC</u>	<u>YEAR</u>
S/NO₃	Method A												
WH	0.33	0.49	0.63	0.94	1.21	1.35	1.45	1.65	1.36	1.02	0.71	0.49	1.03
IT	0.40	0.44	0.63	0.90	1.07	1.38	1.57	1.66	1.26	0.91	0.74	0.48	1.01
PS	0.45	0.58	0.77	0.95	1.08	1.40	1.56	1.59	1.18	0.91	0.76	0.63	1.05
VA	0.73	0.80	0.91	1.06	1.14	1.39	1.41	1.59	1.44	1.00	0.80	0.81	1.16
IL	0.91	0.93	1.02	1.03	1.14	1.27	1.38	1.36	1.36	1.15	1.13	0.87	1.17
BR	1.21	1.10	1.12	1.18	1.08	1.17	1.13	1.07	1.17	1.04	1.04	0.93	1.11
LE	0.85	1.06	1.38	1.19	1.27	1.18	1.28	1.49	1.44	1.24	1.01	1.02	1.24
OX	0.85	0.96	0.99	1.11	1.49	1.32	1.52	1.57	1.19	1.22	1.16	1.06	1.25
OR	1.41	1.48	1.48	1.39	1.32	1.37	1.48	1.58	1.58	1.65	1.37	1.35	1.45
S/NO₃	Method B												
WH	0.53	0.71	0.76	1.08	1.27	1.41	1.48	1.76	1.54	1.13	0.85	0.61	1.17
IT	0.54	0.57	0.70	0.96	1.12	1.41	1.66	1.77	1.34	1.00	0.89	0.55	1.09
PS	0.58	0.71	0.88	1.01	1.15	1.43	1.59	1.66	1.26	1.02	0.89	0.84	1.11
VA	0.95	1.00	1.03	1.13	1.13	1.49	1.39	1.63	1.53	0.95	0.94	0.94	1.20
IL	1.32	1.06	1.18	1.07	1.17	1.34	1.42	1.45	1.47	1.25	1.23	1.04	1.26
BR	2.00	1.61	1.57	1.67	1.24	2.30	1.13	1.23	1.36	1.46	1.41	1.53	1.58
LE	1.35	2.51	1.70	1.99	1.35	1.25	2.82	1.70	2.07	2.05	1.55	1.54	1.81
OX	1.25	1.15	1.13	1.29	1.60	1.40	1.59	1.62	1.37	1.22	1.37	1.29	1.38
OR	2.08	1.97	1.63	1.41	1.39	1.40	1.39	1.62	1.62	1.72	1.59	1.83	1.63
S/NO₃	Method C												
WH	0.41	0.58	0.70	1.01	1.21	1.34	1.41	1.60	1.43	1.00	0.76	0.53	1.00
IT	0.44	0.47	0.66	0.89	1.08	1.35	1.56	1.67	1.26	0.96	0.78	0.46	0.92
PS	0.49	0.58	0.80	0.96	1.12	1.38	1.53	1.59	1.21	0.95	0.82	0.65	0.98
VA	0.82	0.84	0.99	1.09	1.11	1.44	1.32	1.54	1.47	0.91	0.91	0.88	1.11
IL	1.16	1.01	1.11	1.04	1.14	1.29	1.36	1.37	1.42	1.21	1.17	0.86	1.19
BR	1.61	1.40	1.41	1.53	1.17	1.42	1.06	1.17	1.29	1.33	1.24	1.28	1.33
LE	1.14	1.59	1.55	1.62	1.28	1.20	1.30	1.58	1.81	1.64	1.34	1.32	1.45
OX	1.02	0.97	1.05	1.18	1.51	1.35	1.55	1.56	1.28	1.18	1.25	1.10	1.27
OR	1.57	1.63	1.53	1.36	1.33	1.35	1.35	1.59	1.57	1.64	1.47	1.67	1.50

TABLE 15. (contd)

SITE	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YEAR
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SSCS/NO₃ Method A

WH	0.32	0.48	0.63	0.93	1.20	1.35	1.44	1.65	1.36	1.01	0.70	0.48	1.02
IT	0.40	0.43	0.62	0.90	1.07	1.37	1.57	1.65	1.26	0.91	0.73	0.48	1.01
PS	0.44	0.57	0.76	0.94	1.08	1.39	1.55	1.59	1.17	0.90	0.74	0.62	1.04
VA	0.70	0.77	0.89	1.05	1.13	1.39	1.40	1.58	1.42	0.98	0.78	0.80	1.14
IL	0.90	0.92	1.01	1.02	1.14	1.26	1.37	1.35	1.35	1.15	1.11	0.86	1.16
BR	1.03	0.92	0.97	1.06	1.03	1.14	1.10	1.04	1.12	0.90	0.87	0.78	1.02
LE	0.69	0.70	0.96	1.00	1.14	1.11	1.25	1.46	1.22	0.94	0.75	0.77	1.06
OX	0.84	0.94	0.98	1.10	1.48	1.31	1.51	1.56	1.19	1.21	1.14	1.05	1.24
OR	1.39	1.46	1.46	1.36	1.30	1.36	1.47	1.57	1.57	1.63	1.34	1.33	1.4

SSCS/NO₃ Method B

WH	0.53	0.69	0.75	1.07	1.26	1.40	1.47	1.75	1.52	1.12	0.84	0.60	1.16
IT	0.53	0.56	0.69	0.95	1.12	1.40	1.65	1.76	1.34	0.99	0.88	0.54	1.08
PS	0.57	0.69	0.87	1.00	1.14	1.42	1.58	1.65	1.24	1.01	0.87	0.83	1.10
VA	0.92	0.94	1.01	1.11	1.12	1.48	1.38	1.62	1.50	0.93	0.91	0.92	1.18
IL	1.30	1.04	1.17	1.07	1.16	1.33	1.41	1.44	1.47	1.24	1.21	1.03	1.25
BR	1.66	1.18	1.29	1.45	1.14	2.23	1.09	1.19	1.23	1.09	1.10	1.12	1.35
LE	1.00	1.22	1.14	1.47	1.17	1.16	2.16	1.64	1.19	1.39	1.02	1.14	1.33
OX	1.23	1.13	1.11	1.27	1.59	1.39	1.59	1.61	1.36	1.21	1.36	1.27	1.37
OR	2.06	1.95	1.61	1.38	1.36	1.38	1.39	1.61	1.61	1.70	1.56	1.80	1.61

SSCS/NO₃ Method C

WH	0.40	0.57	0.68	1.00	1.19	1.33	1.40	1.59	1.42	0.99	0.75	0.52	0.99
IT	0.43	0.46	0.64	0.88	1.08	1.34	1.55	1.66	1.25	0.95	0.77	0.46	0.92
PS	0.47	0.56	0.79	0.95	1.11	1.37	1.52	1.58	1.19	0.94	0.80	0.64	0.96
VA	0.79	0.80	0.96	1.07	1.10	1.43	1.30	1.53	1.44	0.88	0.88	0.86	1.08
IL	1.14	1.00	1.10	1.03	1.13	1.28	1.35	1.36	1.41	1.20	1.16	0.85	1.18
BR	1.31	1.09	1.15	1.34	1.08	1.35	1.01	1.13	1.18	1.04	0.99	0.99	1.14
LE	0.87	0.82	1.04	1.28	1.14	1.11	1.25	1.51	1.13	1.00	0.94	0.88	1.10
OX	1.00	0.96	1.04	1.17	1.50	1.35	1.55	1.55	1.28	1.17	1.24	1.09	1.25
OR	1.55	1.61	1.51	1.33	1.31	1.34	1.34	1.57	1.56	1.62	1.44	1.64	1.48

FIGURE 7. 1977 Through 1985 AMWA SSCS/Nitrate Ratio for Brookhaven, Calculated Via the Three Methods Described in the Text

FIGURE 8. 1977 Through 1985 AMWA SSCS/Nitrate Ratio for Lewes, Calculated Via the Three Methods Described in the Text

FIGURE 9. Comparison of 1977 Through 1985 AMWA Sulfur/Nitrate Ratio Calculated by Method C (see text) for Brookhaven: Sulfur Versus SSCS

FIGURE 10. Comparison of 1977 Through 1985 AMWA Sulfur/Nitrate Ratio Calculated by Method C (see text) for Lewes: Sulfur Versus SSCS

Annual precipitation weighted averages, similarly calculated, are listed in Table 16 for the 1977 through 1985 period. As was noted by Dana and Easter,⁽³⁾ temporal trends, if indicated, are of low statistical significance. Annual averages for the sulfur/nitrate ratio (Method A) are shown in Figures 11 and 12. A slight decrease with time is possibly reflective of the leveling off or slight decrease in SO₂ emissions, relative to NO₃ emissions during the 1977 through 1985 period.

TABLE 16. Annual Weighted Averages, 1977 Through 1985

SPECIES	YR	Site								
		WH	IT	PS	VA	IL	BR	LE	OX	OR
S (μM)										
	77	22	29	35	36					
	78	28	35	31	28	34				
	79	20	28	24	23	31	20	22	34	
	80	27	29	34	26	30	26	27	38	
	81	20	37	35	32	34	27	28	31	30
	82	20	29	37	30	32	21	21	33	25
	83	20	29	30	23	26	18	25	27	22
	84	21	26	36	21	30	20	23	27	26
	85	21	29	31	24	26	24	22	26	28
NO ₃ (μM)										
	77	23	29	31	30					
	78	25	32	31	24	28				
	79	20	25	24	18	23	16	18	25	
	80	26	30	31	27	27	26	22	30	
	81	18	31	30	26	25	23	22	25	20
	82	19	31	36	26	26	16	16	23	16
	83	18	26	27	20	24	15	18	22	15
	84	22	28	35	20	29	20	20	24	20
	85	23	35	33	23	23	27	19	24	20
Cl (μM)										
	77	5.3	6.1	5.4	14.7					
	78	5.5	5.1	4.9	10.6	5.3				
	79	4.8	6.1	6.2	6.8	14.3	31	54	7.9	
	80	4.7	4.5	7.4	11.8	6.0	41	75	5.5	
	81	3.0	5.3	9.2	14.0	4.4	32	38	6.7	8.1
	82	2.7	5.2	7.0	8.2	5.9	39	83	5.5	7.0
	83	3.4	4.3	5.6	9.0	4.1	37	90	5.0	5.4
	84	6.7	4.7	5.4	5.4	6.2	31	65	4.8	7.6
	85	4.3	9.2	6.6	6.1	5.1	26	55	5.2	7.0
Anion Sum (μeq)										
	77	53	67	70	81					
	78	89	107	99	91	101				
	79	65	87	79	71	90	87	117	101	
	80	85	92	106	91	92	121	151	113	
	81	62	110	110	105	97	110	115	93	88
	82	62	94	117	94	96	96	140	94	73
	83	61	88	92	75	80	87	157	81	65
	84	71	84	113	67	96	91	131	84	80
	85	69	102	103	77	79	101	118	81	82

TABLE 16. (contd)

SPECIES	YR	Site								
		WH	IT	PS	VA	IL	BR	LE	OX	OR
H (μM)										
	77	47	70	77	71					
	78	59	85	79	67	62				
	79	50	69	59	62	56	44	47	68	
	80	61	66	75	55	53	49	48	66	
	81	37	71	58	58	49	45	47	54	53
	82	42	64	69	61	50	39	35	53	48
	83	44	67	73	51	51	40	47	53	43
	84	42	58	79	46	51	42	43	56	47
	85	42	56	65	44	43	49	36	49	50
NH ₄ (μM)										
	77	11	13	15	16					
	78	17	16	14	12	24				
	79	11	15	14	10	21	11.2	12	19	
	80	17	17	16	17	22	18.0	15	25	
	81	12	17	25	16	22	12.3	16	20	13.1
	82	11	15	20	15	19	7.5	10	16	9.1
	83	11	16	13	13	15	6.8	12	16	8.4
	84	14	14	17	11	22	9.4	12	17	14.3
	85	13	19	19	13	18	15.4	12	16	11.5
Na (μM)										
	77	1.2	1.3	2.2						
	78	1.9	2.1	2.4	3.7	2.4				
	79	2.4	2.4	3.5	4.7	4.5	26	54	3.6	
	80	2.1	2.3	4.2	9.2	4.1	36	61	3.1	
	81	1.3	2.2	6.2	11.7	1.7	27	32	4.4	5.5
	82	1.9	2.3	5.3	5.1	3.5	35	64	4.1	4.7
	83	2.1	1.4	2.6	5.5	2.6	32	76	2.5	2.9
	84	2.4	1.6	2.3	3.1	3.3	24	51	2.3	6.2
	85	1.4	2.1	2.5	2.9	2.4	24	38	2.5	3.5
Cation Sum (μeq)										
	77	52	64	71						
	78	92	113	103	91	112				
	79	69	92	84	81	100	89	132	103	
	80	86	93	109	90	99	122	149	113	
	81	56	98	105	95	88	96	109	90	81
	82	59	87	107	86	88	93	127	82	68
	83	62	90	92	77	82	89	157	81	64
	84	65	80	106	64	94	85	123	83	77
	85	62	82	93	62	72	98	103	73	72

TABLE 16. (contd)

SPECIES	YR	Site								
		WH	IT	PS	VA	IL	BR	LE	OX	OR
S/NO ₃ (M)										
	77	0.97	1.00	1.11	1.23					
	78	1.12	1.08	1.01	1.17	1.19				
	79	1.03	1.12	1.00	1.32	1.36	1.21	1.23	1.32	
	80	1.06	0.95	1.08	0.99	1.09	1.00	1.23	1.26	
	81	1.10	1.18	1.16	1.26	1.35	1.16	1.26	1.25	1.54
	82	1.05	0.94	1.03	1.13	1.25	1.28	1.29	1.46	1.56
	83	1.11	1.09	1.09	1.18	1.07	1.19	1.40	1.25	1.47
	84	0.97	0.93	1.04	1.06	1.06	1.02	1.14	1.12	1.33
	85	0.90	0.82	0.96	1.06	1.13	0.92	1.16	1.09	1.38
SSCS (μM)										
	77	22	29	35	36					
	78	28	34	31	28	34				
	79	20	27	24	23	31	18	19	33	
	80	27	29	33	26	29	24	24	38	
	81	20	36	35	32	33	26	26	31	30
	82	20	29	37	29	32	19	17	33	25
	83	20	29	29	23	25	16	21	27	22
	84	21	26	36	21	30	18	20	27	26
	85	21	29	31	24	26	23	19	26	
SSCS (%)										
	77	0.4	0.2	0.3	0.4					
	78	0.6	0.6	0.5	1.1	0.6				
	79	0.8	0.7	1.0	1.3	1.1	8.2	14.3	0.7	
	80	0.5	0.6	1.0	2.2	1.0	8.2	10.2	0.6	
	81	0.5	0.6	1.2	2.3	0.5	6.0	7.0	0.9	1.4
	82	0.6	0.7	0.9	1.2	0.7	10.1	18.3	0.8	1.3
	83	0.9	0.6	0.7	1.9	0.7	10.6	17.0	0.7	1.0
	84	1.0	0.7	0.7	1.1	0.8	7.7	14.3	0.7	1.4
	85	0.5	0.9	0.7	1.0	0.7	5.8	14.1	0.8	0.9
Precipitation (cm)										
	77	125	106	122	71					
	78	84	86	97	109	64				
	79	112	112	137	134	46	111	143	95	
	80	96	97	88	87	92	84	96	99	
	81	123	123	104	88	97	107	90	79	104
	82	96	95	100	98	94	113	104	111	156
	83	137	109	115	152	99	167	158	106	124
	84	114	125	124	128	82	149	121	106	138
	85	124	87	100	109	110	94	115	114	117

FIGURE 11. Annual Weighted Average Sulfur/Nitrate Ratio (μM) for Whiteface, Ithaca, Penn State, and Virginia

FIGURE 12. Annual Weighted Average Sulfur/Nitrate Ratio (μM) for Illinois, Brookhaven, Lewes, Oxford, and Oak Ridge

4.0 EXTERNAL QUALITY ASSURANCE: USGS BLIND SAMPLE RESULTS

Laboratory external quality assurance for MAP3S/PCN is provided through an arrangement with the U.S. Geological Survey (USGS), which conducts a near-identical service for the NADP/NTN network.⁽¹³⁾ The procedure involves submission to the sites, by USGS, of standard solutions of known concentrations of the major species analyzed; the site operators then transfer the samples to PCN shipping bottles and submit to PCL with actual precipitation samples. Fictitious sample identification and field data are assigned to the samples, so that PCL personnel are unaware of the actual identity of the samples. Postcards with the identification information are submitted to USGS and an independent QA clerk at PNL; when analyses results are ready for quarterly reporting, the blind samples are identified, and their concentrations removed from the computer data base and reported to USGS.

All but one of the quality assurance samples used during 1985 are USGS Standard Reference Water Samples (SRWS); their concentrations are known as "most probable values" on the basis of analyses performed by numerous laboratories. Table 17 lists the USGS identifications, dilution factors in preparation for submission to the sites, the number of samples of each run through the PCN system, and the dilution concentrations.

Figures 13 to 18 are plots of the PCL concentration values compared to the USGS values for the six major species that are considered stable for external blind sample analyses purposes. Included on the figures are best-fit linear regression lines, and the r^2 values. The results are summarized in Table 18 in terms of accuracy and bias (as defined in Section 2.3.1), under the assumption that the most probable values are true. For comparison, also shown are accuracy values for two co-located sampling studies conducted under the Sulfate Regional Experiment (SURE) and Utility Acid Precipitation Study Program (UAPSP) projects.⁽¹⁶⁾ The co-located samples results can be considered to represent a measure of the variances associated with both field sample handling and laboratory analysis. The trends in the magnitudes of the accuracies among the species are comparable, suggesting that the external blind sample variances are compatible with normal laboratory expectations for the included species.

TABLE 17. Standard USGS Solutions Provided Blind Via Sites to PCL

USGS ID#	DIL FAC	Diluted Concentration (μM)							
		N	Ca	Mg	Na	K	Cl	SO ₄	NO ₃
74	20	2	9.35	4.00	6.00	11.95	1.95	7.45	8.70
80	25	2	49.52	20.24	55.64	4.48	35.56	30.16	1.56
80	50	1	24.76	10.12	27.82	2.24	17.78	15.08	0.78
80	100	3	12.38	5.06	13.91	1.12	8.89	7.54	0.39
82	20	1	17.25	7.40	13.75	2.40	3.70	14.60	0.00
82	25	2	13.80	5.92	11.00	1.92	2.96	11.68	0.00
82	50	2	6.90	2.96	5.50	0.96	1.48	5.84	0.00
84	100	2	21.63	21.31	34.65	1.21	14.10	36.16	2.81
84	150	2	14.42	14.21	23.10	0.81	9.40	24.11	1.87
84	200	1	10.82	10.66	17.33	0.61	7.05	18.08	1.41
84	250	1	8.65	8.52	13.86	0.48	5.64	14.46	1.12
86	50	2	35.68	23.28	67.14	2.36	25.04	45.78	5.64
86	100	1	17.84	11.64	33.57	1.18	12.52	22.89	2.82
86	200	1	8.92	5.82	16.79	0.59	6.26	11.45	1.41
88	150	1	23.95	14.81	34.78	0.87	6.96	37.92	1.70
88	200	3	17.97	11.11	26.09	0.65	5.22	28.44	1.28
910000	2	5	3.10	1.15	6.18	2.00	12.80	4.06	6.65

FIGURE 13. Comparison of USGS and PCL Concentration (μM) Determinations for 1985 External QA Samples: Calcium. The solid line is a least-squares fit ($R^2 = 0.45$).

FIGURE 14. Comparison of USGS and PCL Concentration (μM) Determinations for 1985 External QA Samples: Magnesium. The solid line is a least-squares fit ($R^2 = 0.90$).

FIGURE 15. Comparison of USGS and PCL Concentration (μM) Determinations for 1985 External QA Samples: Sodium. The solid line is a least-squares fit ($R^2 = 0.83$).

FIGURE 16. Comparison of USGS and PCL Concentration (μM) Determinations for 1985 External QA Samples: Potassium. The solid line is a least-squares fit ($R^2 = 0.88$).

FIGURE 17. Comparison of USGS and PCL Concentration (μM) Determinations for 1985 External QA Samples: Chloride. The solid line is a least-squares fit ($R^2 = 0.88$).

FIGURE 18. Comparison of USGS and PCL Concentration (μM) Determinations for 1985 External QA Samples: Sulfate. The solid line is a least-squares fit ($R^2 = 0.97$).

TABLE 18. Summary of External Blind Sample Results for 1985

Species	Concentration, μM				Accuracy, %	Bias, %	Co-Located Accuracy, %	
	Mean		MED				Sure	UAPSP
	USGS	PCN	USGS	PCN				
SO ₄	18	18	15	12	6.2	-1.5	5.3	3.8
Na	22	21	15	14	8.4	2.0	27	6.9
Mg	9.6	9.0	8.0	5.5	7.8	0.0	12	9.6
K	2.2	2.4	1.2	1.4	29	5.0	45	24
Cl	11	13	13	12	12	-9.4	13	5.4
Ca	16	20	15	14	11	-0.9	18	16

FIGURE 18. Comparison of 1985 and 1986 Concentration (X) to 1985 results (Y) for 1985 (X-axis) and 1986 (Y-axis) data. The solid line is a least-squares fit ($r^2 = 0.97$).

TABLE 18. Summary of Estimated 1986 Sample Results for 1985

Species	Concentration, $\mu\text{g/g}$		Accuracy, %	Bias, %	Co-located Accuracy, %	
	1985	1986			1985	1986
SO ₄	18	18	0.0	-1.5	5.3	-3.8
Fe	25	21	-8.4	3.0	2.7	6.3
Mn	0.0	0.0	0.0	0.0	1.3	0.0
K	2.5	2.4	2.0	0.0	0.0	2.2
Cl	11	13	17	-0.4	1.9	0.4
Ca	18	12	-33	-0.0	1.0	1.0

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APPENDIX A

QUALITY CONTROL DESCRIPTORS

APPENDIX A

QUALITY CONTROL DESCRIPTORS

The primary function of the Precipitation Chemistry Laboratory is chemical analysis of precipitation samples collected by monitoring networks administered by the Atmospheric Sciences Department of Pacific Northwest Laboratory (PNL). Attendant to this function are sample identification, custody and control, supply of field operations, computer data entry, and fulfillment of PNL and sponsor quality control and assurance requirements. Assurance of uniformity of performance of the various tasks is facilitated through the use of written standard operating procedures, here named quality control descriptors, or QCDs. These procedures, which are intended to be integral components of the formal QA plan, cover all major laboratory activities, and are designed to be training tools for new personnel as well as reference manuals and standards for performance. Laboratory procedures change continuously as new analytical methods are introduced and as network priorities are modified. Thus, the QCDs are frequently reviewed for current applicability and modified as necessary.

Table A.1 is a list of current QCDs; subsequent tables and figures are excerpts from these, as referenced in the main text of this report. Complete copies of QCDs may be obtained from the author.

TABLE A.1. Quality Control Descriptors for the MAP3S/PCN

<u>Number</u>	<u>Quality Control Descriptor Title</u>
<u>Sample Identification and Custody</u>	
1.	Sample Receipt and Login
2.	Field Data Receipt, Filing and Login
<u>Chemical Analysis</u>	
3.	pH and Conductivity
4.	Ion Chromatography
5.	Automated Wet Chemistry
6.	Atomic Absorption Spectrometry
7.	Inductively Coupled Plasma Spectrometry
8.	Alkalinity, Total Acidity, and Gran Titration
<u>Data Base Formation and Quality Control</u>	
9.	Analytical Results Login, QC Checks and Clearance
10.	PCN Data Login Procedures
11.	Computer Data Checks
12.	External QA Clearance, Refiling and Archival
13.	Computer Data Reporting
<u>MAP3S Network Supply and QA</u>	
14.	Equipment Supply for MAP3S
15.	Shipping Procedure for MAP3S/PCN
16.	Preparation of the MAP3S/PCN pH Test/Samples
17.	Preparation of the MAP3S/PCN Field Blank Samples
18.	Procedures for Recording Information in the MAP3S/PCN "Out Book"
19.	MAP3S/PCN Site Audits
20.	Site Operator's Manual

APPENDIX B

DATA EDITING PROCEDURE

APPENDIX B

DATA EDITING PROCEDURE

TABLE B.1. Procedures for Editing of PCL Data for Statistical Calculations

A. DEFINITIONS OF CALCULATED PARAMETERS

1. PRECIPITATION (cm). The greater of sample volume or predicted volume divided by collector area.
2. COLLECTION EFFICIENCY. The ratio of sample volume to predicted volume.
3. TIME (year). Time of collection of sample in years since January 1, 1976.

B. GENERAL EDIT ROUTINE (LISTED IN ORDER OF PRIORITY FOR ACTION)

1. If precipitation is missing (both volumes missing), sample is removed. Number of samples thus removed is counted.
2. If collection efficiency exists (both volumes exist), and is less than 0.5, sample is removed and numbers so removed counted. (Sample is retained if one of volumes is missing.)
3. If concentration (or other parameter of interest) is missing, sample is removed and numbers so removed counted.
4. If concentration is below minimum detection limit (MDL), concentration is set to MDL/2.

NOTE: This has no effect on averages for major species. Minor species such as 'SO₂' or 'K⁺' could be significantly affected by this action, so caution should be taken.

Each of the above four steps may be bypassed, according to the particular application.

For weighted averaging, ALL FOUR are operative.

TABLE B.1. (contd)

C. ADDITIONAL NOTES ON WEIGHTED AVERAGES

1. Total precipitation (for samples before the general edit) is compared with precipitation for those samples surviving the edit. If the latter is less than 80% of the former, the weighted average is replaced by "IPC" (insufficient precipitation coverage).
2. Precipitation reported is total precipitation (pre-edit), but all weighting is done with post-edit precipitation.
3. Averages for periods with less than two events available for averaging are not reported.

APPENDIX C

SEA-SALT CORRECTED SULFATE ALGORITHM

APPENDIX C

SEA-SALT CORRECTED SULFATE ALGORITHM

Sea salt contains large amounts of Na^+ , Cl^- , Mg^{++} , Ca^{++} , K^+ and S, in relatively constant ratios. When sea-salt particles enter precipitation samples, they raise the concentrations of these ions over those which existed prior to the presence of sea salt. In order to determine the $\text{SO}_4^{=}$ concentration in precipitation without the influence of sea salt, it is necessary to correct the measured $\text{SO}_4^{=}$ concentration for the sea-salt contribution. ADS uses the following procedures to correct individual sample $\text{SO}_4^{=}$ concentrations for sea-salt contribution. Sea-salt corrections are made only for coastal sites.

Ratios of Na^+ , Cl^- and Mg^{++} ions measured in a precipitation sample are compared to the same ratios in sea water to see which ions provide the best indication of sea-salt influence. The following three ratios are currently used:

$$\text{MN} = \frac{\text{Mg}^{++}/\text{Na}^+ \text{ precipitation measured}}{\text{Mg}^{++}/\text{Na}^+ \text{ sea salt}}$$

where $\text{Mg}^{++}/\text{Na}^+ = 0.119$ is the sea-salt mass ratio

$$\text{NC} = \frac{\text{Na}^+/\text{Cl}^- \text{ precipitation measured}}{\text{Na}^+/\text{Cl}^- \text{ sea salt}}$$

where $\text{Na}^+/\text{Cl}^- = 0.557$ is the sea-salt mass ratio

$$\text{MC} = \frac{\text{Mg}^{++}/\text{Cl}^- \text{ precipitation measured}}{\text{Mg}^{++}/\text{Cl}^- \text{ sea salt}}$$

where $\text{Mg}^{++}/\text{Cl}^- = 0.067$ is the sea-salt mass ratio

These ratios are used to determine whether $\text{SO}_4^{=}$ is corrected for sea-salt influence using Na^+ or Mg^{++} .

Sulfate corrected for sea salt is determined by

$$SO_{4C}^{\bar{}} = SO_4^{\bar{}} - 0.25 Na^+ \quad (1)$$

if correction is based on Na^+ and

$$SO_{4C}^{\bar{}} = SO_4^{\bar{}} - 2.09 Mg^{++} \quad (2)$$

if correction is based on Mg^{++} . All concentrations are in mg/L. In the situation when either Na^+ or Mg^{++} is not available for a precipitation sample, then the correction is based on the one available. In the event that neither are available, no sea-salt correction is made and the measured $SO_4^{\bar{}}$ concentration is used as if a correction had been made.

The following algorithm is applied to determine whether $SO_4^{\bar{}}$ is corrected for sea salt using Na^+ (Equation 1) or using Mg^{++} (Equation 2). The algorithm assumes that all precipitation measured $SO_4^{\bar{}}$ concentrations are to be corrected for sea salt. The algorithm attempts to account for the presence of confounding influences (i.e., non-sea salt) on precipitation measured Na^+ , Mg^{++} and Cl^- concentrations.

Algorithm

- I. If $SO_4^{\bar{}}$ is missing, then $SO_{4C}^{\bar{}}$ is missing.
- II. If $SO_4^{\bar{}}$ is present, then complete the following steps.
 - A. If Na^+ and Mg^{++} are both missing, then $SO_{4C}^{\bar{}} = SO_4^{\bar{}}$.
 - B. If Mg^{++} is present and Na^+ is missing, then $SO_{4C}^{\bar{}} = SO_4^{\bar{}} - 2.09 Mg^{++}$.
 - C. If Mg^{++} is missing and Na^+ is present, then $SO_{4C}^{\bar{}} = SO_4^{\bar{}} - 0.25 Na^+$.
 - D. If Na^+ and Mg^{++} are both present, then
 1. when $0.75 \leq MN \leq 1.25$, set $SO_{4C}^{\bar{}} = SO_4^{\bar{}} - 0.25 Na^+$
 2. otherwise, compute ratios MC and NC.

- a. If Cl^- is missing, then $\text{SO}_4^{\bar{\bar{C}}} = \text{SO}_4^= - 0.25 \text{ Na}^+$.
- b. If $0.75 \leq \text{MC} \leq 1.25$ and $(\text{NC} < 0.75 \text{ or } \text{NC} > 1.25)$, then $\text{SO}_4^{\bar{\bar{C}}} = \text{SO}_4^= - 2.09 \text{ Mg}^{++}$.
- c. If $0.75 \leq \text{NC} \leq 1.25$ and $(\text{MC} < 0.75 \text{ or } \text{MC} > 1.25)$, then $\text{SO}_4^{\bar{\bar{C}}} = \text{SO}_4^= - 0.25 \text{ Na}^+$.
- d. Otherwise check if
 - i) if $|\text{NC} - 1| \leq |\text{MC} - 1|$, then $\text{SO}_4^{\bar{\bar{C}}} = \text{SO}_4^= - 0.25 \text{ Na}^+$
 - ii) otherwise $\text{SO}_4^{\bar{\bar{C}}} = \text{SO}_4^= - 2.09 \text{ Mg}^{++}$.

The sea-salt composition mass ratios are from a technical report: Rahn, K. A. 1976. "The Chemical Composition of the Atmospheric Aerosol." Graduate School of Oceanography, University of Rhode Island, Kingston, Rhode Island.

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