The MAP3S Precipitation Chemistry Network:

**Data and Quality Control Summary
for 1986 and 1987**

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THE MAP3S PRECIPITATION CHEMISTRY NETWORK: DATA
AND QUALITY CONTROL SUMMARY FOR 1986 AND 1987

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PREFACE

This report is the tenth in a series of periodic summary reports of the MAP3S Precipitation Chemistry Network (PCN). Beginning with the summary for 1985, 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 authors.

A great number of persons have contributed to the operation of the PCN and interpretation of results over the 11 years of the network's history; their efforts are greatly appreciated, but space permits listing only those active during the period from 1986 to the present writing:

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EXECUTIVE SUMMARY

This report, the tenth 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 years 1986 and 1987 individually and for the period 1977 through 1987. In addition, external quality assurance results for 1986 and 1987 are summarized.

CONTENTS

PREFACE	iii
EXECUTIVE SUMMARY	v
1.0 INTRODUCTION	1.1
2.0 QUALITY CONTROL	2.1
2.1 INTRODUCTION	2.1
2.2 SAMPLE QUALITY MEASURES	2.1
2.3 LABORATORY QUALITY CONTROL	2.9
3.0 DATA SUMMARY FOR 1986, 1987, AND 1977 THROUGH 1987	3.1
3.1 INTRODUCTION	3.1
3.2 EDITING STATISTICS	3.1
3.3 DISTRIBUTION AND PRECIPITATION-WEIGHTED STATISTICS	3.6
3.4 TEMPORAL TRENDS	3.18
4.0 EXTERNAL QUALITY ASSURANCE	4.1
5.0 REFERENCES	5.1
APPENDIX A - STANDARD OPERATING PROCEDURES	A.1
APPENDIX B - SITE AUDITS FOR 1986 AND 1987	B.1
APPENDIX C - DATA EDITING PROCEDURE	C.1

FIGURES

1.1	Locations of the MAP3S Precipitation Chemistry Network Sites	1.1
2.1	Accuracy, Bias, and Precision Estimates for Chemical Analyses from 1986-1987 QC Check Sample Data	2.11
3.1	Mean Number of Samples Per Site Per Year	3.4
3.2	Percent of Samples Removed from Total Network Statistics Data Base Because of Missing Rainfall, Low Collection Efficiency, and Missing Chemical Results	3.4
3.3	Comparison of Missing Chemistry Values for Sodium and Sulfate: Total Network Statistics Data Base	3.6
3.4	Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Whiteface	3.28
3.5	Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Ithaca	3.29
3.6	Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Penn State	3.29
3.7	Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Virginia	3.30
3.8	Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Illinois	3.30
3.9	Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Brookhaven	3.31
3.10	Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Lewes	3.31
3.11	Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Oxford	3.32
3.12	Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Oak Ridge	3.32
4.1	Comparison of PCL Values and USGS Most Probable Values for Calcium	4.2
4.2	Comparison of PCL Values and USGS Most Probable Values for Chloride	4.3

4.3	Comparison of PCL Values and USGS Most Probable Values for Magnesium	4.3
4.4	Comparison of PCL Values and USGS Most Probable Values for Potassium	4.4
4.5	Comparison of PCL Values and USGS Most Probable Values for Sodium	4.4
4.6	Comparison of PCL Values and USGS Most Probable Values for Ammonium	4.5
4.7	Comparison of PCL Values and USGS Most Probable Values for Sulfate	4.5

TABLES

1.1	Network Site Details	1.2
1.2	List of Previous MAP3S Annual Summary Reports	1.3
1.3	Chemical Species and Analysis Details	1.4
2.1	Quality Control Measure Statistics for 1986	2.4
2.2	Quality Control Measure Statistics for 1987	2.6
2.3	Quality Control Measure Statistics for 1977 Through 1987	2.7
2.4	Laboratory Quality Control Summary for 1986 and 1987	2.10
3.1	Editing Statistics for Sea-Salt Corrected Sulfur Distribution Calculations	3.2
3.2	Editing Statistics for Sodium Distribution Calculations	3.5
3.3	Distribution Statistics for 1986	3.7
3.4	Distribution Statistics for 1987	3.10
3.5	Distribution Statistics for 1977 Through 1987	3.13
3.5b	Distribution Statistics for SSCS for Accumulated Seasons	3.16
3.6	Monthly Weighted Averages for 1986	3.19
3.7	Monthly Weighted Averages for 1987	3.21
3.8	Accumulated Monthly Weighted Averages for 1977 Through 1987	3.23
3.9	Annual Weighted Averages	3.25
3.10	Trend Statistics for SSCS: 1977 Through 1987	3.27
4.1	External Blind Samples Analyzed During 1986 and 1987, and USGS Most Probable Concentration Values	4.1
4.2	Summary of External Blind Samples Results	4.6

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 (Watson and Olsen 1984). Pacific Northwest Laboratory's (PNL) responsibilities are site supply and auditing, chemical and data analyses, reporting, and general network management. The site operations are funded by separate contracts between the U.S. Department of Energy and 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 1.1 is a map showing the locations of the sampling sites, and Table 1.1 gives

FIGURE 1.1. Locations of the MAP3S Precipitation Chemistry Network Sites

TABLE 1.1. Network Site Details

Site Number	Name	Location		Elevation (m, asl)	Date of First Sample Collected	Participating Organization
		Longitude	Latitude			
1	Whiteface	73° 51'	44° 23'	685	October 11, 1976	Atmospheric Sciences Research Center State University of New York at Albany
2	Ithaca	76° 43'	42° 23'	583	October 26, 1976	Section of Ecology and Systematics Cornell University
3	Penn State	77° 57'	46° 47'	396	September 22, 1976	Department of Meteorology Pennsylvania State University
4	Virginia	78° 32'	38° 02'	171	December 12, 1976	Department of Environmental Sciences University of Virginia
5	Illinois	88° 22'	46° 03'	213	November 28, 1977	Illinois State Water Survey Champaign, Illinois
6	Brookhaven	72° 53'	46° 52'	24	February 9, 1978	Atmospheric Sciences Division Brookhaven National Laboratory
7	Lewes	75° 06'	38° 46'	8	March 1, 1978	College of Marine Studies University of Delaware
8	Oxford	84° 44'	39° 32'	283	October 1, 1978	Institute of Environmental Sciences Miami University
9	Oak Ridge	84° 17'	35° 58'	338	January 7, 1981	Oak Ridge National Laboratory

organizational and location details. More details on the network operation may be found in open-literature publications (MAP3S/RAINE Research Community 1982; Dana and Easter 1987), a quality control report (MAP3S 1980a), and past periodic summary reports (PSR) (Table 1.2). The seventh in the latter series (Rothert and Dana 1984) contains a history of the PCN (through 1983), and the most recent (Dana 1988) contains a detailed summary of quality control activities.

A major objective of the PCN is the chemical analysis of precipitation samples for the major ionic species. Table 1.3 is a list of the species, methods, instruments, detection limits, and goals for measurement uncertainty. Over the course of 11 years of operation, several analysis methods have changed, as have basic detection limits and estimated errors. Shown in the

TABLE 1.2. List of Previous MAP3S Annual Summary Reports

<u>Author</u>	<u>Date</u>	<u>Title</u>	<u>PNL No.</u>
MAP3S	1977	The MAP3S Precipitation Chemistry Network: First Periodic Summary Report (September 1976-June 1977)	PNL-2402
MAP3S	1978	The MAP3S Precipitation Chemistry Network: Second Periodic Summary Report (July 1977-June 1978)	PNL-2829
MAP3S	1980b	The MAP3S Precipitation Chemistry Network: Third Periodic Summary Report (July 1978-December 1979)	PNL-3400
MAP3S	1981	The MAP3S Precipitation Chemistry Network: Fourth Periodic Summary Report (January 1980-December 1980)	PNL-4144
Dana and Rothert	1983	The MAP3S Precipitation Chemistry Network: Fifth Periodic Summary Report (January 1981-December 1981)	PNL-4599
Dana and Rothert	1984	The MAP3S Precipitation Chemistry Network: Sixth Periodic Summary Report (January 1982-December 1982)	PNL-4787
Rothert and Dana	1984	The MAP3S Precipitation Chemistry Network: Seventh Periodic Summary Report (1983)	PNL-5298
Dana	1987	The MAP3S Precipitation Chemistry Network: Eighth Periodic Summary Report (1984)	PNL-6055
Dana	1988	The MAP3S Precipitation Chemistry Network: Ninth Periodic Summary Report (1985)	PNL-6461

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 (Watson and Olsen 1984).

Beginning with the PSR for 1985, quality control activities and an annual summary of data analyses for the current year and all previous years are given

TABLE 1.3. Chemical Species and Analysis Details

Species	Method ^(a)	Instrument	Minimum Detection Limit (μ M) ^(b)	Quantitative Detection Limit (μ M) ^(c)	Estimated Error ^(d)
H ⁺ (free)	Electrode	Corning® Model 135 pH/Ion Meter	--	--	+0.05 pH units ^(e)
Conductivity	Bridge	Markson Electromark®	1.20	--	+20%
SO ₃ ⁼	AWC	Alpkem® Auto Analyzer	0.10	0.20	+GD (QDL or 10%)
SO ₄ ⁼	IC	Dionex™ System 4000i (Anion)	0.03	0.20	+GD (QDL or 10%)
NO ₃ ⁻	IC	Dionex™ System 4000i (Anion)	0.05	0.20	+GD (QDL or 10%)
Cl ⁻	IC	Dionex™ System 4000i (Anion)	0.50	2.00	+GD (QDL or 10%)
PO ₄ ³⁻	IC	Dionex™ System 4000i (Anion)	0.05	0.20	+GD (QDL or 10%)
NH ₄ ⁺	IC	Alpkem® Auto Analyzer	0.10	0.50	+GD (QDL or 10%)
Na ⁺	ICAP	Leeman Labs Plasma-Spec® ICP 2.5	0.10	0.40	+GD (QDL or 10%)
K ⁺	ICAP	Leeman Labs Plasma-Spec® ICP 2.5	0.20	0.50	+GD (QDL or 10%)
Ca ⁺⁺	ICAP	Leeman Labs Plasma-Spec® ICP 2.5	0.05	0.20	+GD (QDL or 10%)
Mg ⁺⁺	ICAP	Leeman Labs Plasma-Spec® ICP 2.5	0.00	0.20	+GD (QDL or 10%)

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

(b) Concentrations are expressed in molar units: μ M = μ mol/L.

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

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

(e) At pH = 4.

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in the PSR. Complete data listings (including hourly precipitation amounts) continue to be available via the quarterly reports, from the author or other PNL staff 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 for the summary period. Section 3 summarizes the data for 1986 and 1987 and for the period 1977 through 1987, updating past summaries in PSRs and the journal articles (MAP3S/RAINE Research Community 1982; Dana and Easter 1987). Section 4 describes the 1986 and 1987 results from the external quality assurance, blind sample program administered by the U.S. Geological Survey.

2.0 QUALITY CONTROL

2.1 INTRODUCTION

Quality control (QC) and quality assurance (QA) activities for PCN are guided by a formal QA plan. A major component of the plan is documentation of standard operating procedures [SOP--formerly called quality control descriptors (Rothert and Dana 1984)]; an index of these is provided in Appendix A. Early QA/QC considerations for PCN are documented in an earlier report (Rothert and Dana 1984); among the contents are a description of the site selection process and equipment considerations. Since no new sites have been added since 1981 and there have been no major equipment changes during this reporting period, these topics will not be discussed in this report. Siting and equipment procedures in the PCN are nearly identical to those of the National Atmospheric Deposition Program/National Trends Network (NADP/NTN) (Bigelow 1986; James 1988). Routine site operation is described in the site operator's manual (an SOP--see Appendix A), which is available from the authors. An important aspect of QA/QC is site audits, the conduct of which is a major objective of the PNL network management. Appendix B details site audits conducted during 1986-1987.

The balance of this section will consider general sample quality measures (laboratory and field) and laboratory QC, using the same format as the most recent QC report (Rothert and Dana 1984). The present report, however, does not consider field blank analyses and field pH test results, which were treated in detail previously. The general sample quality measures include ion balance, measured/calculated conductivity difference, and lab/field pH difference. Internal laboratory QC measures include accuracy, bias, and precision estimates for chemical analysis procedures. External QA, conducted through the U.S. Geological Survey (USGS) blind audit program (Schroder, Bricker, and Willoughby 1985), is considered in Section 4.

2.2 SAMPLE QUALITY MEASURES

Three commonly applied measures of QC are ion balance, measured/calculated conductivity difference (or conductivity "balance"), and laboratory/field pH difference. These are not strictly laboratory or field measures, but reflect

elements of the quality level of both types of procedures. Since uncontrolled natural processes can lead to chemical change in precipitation samples between collection and analysis, and species for which no analysis is done may exist in some samples, the results of these measures are not necessarily indicative of the efficacy of laboratory and field procedures. These QC measures can be indicators of problems, especially if trends appear that are not usual in terms of the 11-year history of PCN measurements. The ion balance IB (%) is given by

$$IB = \frac{S_A - S_C}{\left(\frac{S_A + S_C}{2}\right)} \times 100 \quad (2.1)$$

where S_A and S_C are the equivalents totals ($\mu\text{eq/L}$) of anions (sulfate, nitrate, chloride, and phosphate) and cations (hydrogen, ammonium, sodium, potassium, calcium, and magnesium), respectively. The criteria for reanalysis (Peden et al. 1986), or reassessment of acceptability of the samples, are:

<u>If $S_A + S_C$ is:</u>	and	<u> IB is:</u>
<50		>120
50 to 100		>60
≥ 100		>30

Conductivity "balance" CB (%) is

$$CB = \frac{C_C - C_M}{C_M} \times 100 \quad (2.2)$$

where C_M ($\mu\text{mho/cm}$) is measured conductivity and C_C ($\mu\text{mho/cm}$) is

$$\begin{aligned} C_C = & 0.35[\text{H}^+] + 0.2228[\text{H}^+]^{-1} + 0.0759[\text{Cl}^-] + 0.104[\text{Ca}^{2+}] \\ & + 0.0932[\text{Mg}^{2+}] + 0.0489[\text{Na}^+] + 0.0710[\text{NO}_3^-] + 0.1478[\text{SO}_4^{2-}] \\ & + 0.0745[\text{NH}_4^+]; \end{aligned} \quad (2.3)$$

the brackets denote molar concentrations. The criteria for reassessment are (Peden et al. 1986)

<u>If C_B is:</u>	and	<u>C_M is:</u>
>50		<5
>30		5 to 30
>20		>30

Laboratory/field pH difference (pH units) provides an indication of possible sample deterioration or problems with either laboratory or field pH measurement; in general, a difference should be expected (increase in pH) because of the consumption of organic acids by microbes or other processes. The "normal" or expected difference should vary from site to site, and possibly with season.

Tables 2.1, 2.2, and 2.3 contain general statistics for these sample quality measures for individual years 1986 and 1987 and for the period 1977 through 1987. The general statistics procedures are described in Section 3 and Appendix C. Only those samples that have analytical results for all measured species are included in the numbers of samples remaining after editing, as shown in Tables 2.1, 2.2, and 2.3. This number is usually smaller than the numbers given in Section 3 for individual species. Tables 2.1 and 2.3 include data from a portion of the period when pH measurements were biased (October 1985 through July 1986) (Dana 1988). The sub-tables that do not include the biased data show ion balance and lab/field pH difference statistics more in agreement with those of other years than do the sub-tables that include the biased data. The unbiased period, July to December, with fewer samples, shows statistics for ion balance and lab/field pH difference more in agreement with other years and the total data base than does the entire year.

TABLE 2.1. Quality Control Measure Statistics for 1986

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centiles					MAX
									5	25	MED	75	95	
ION BALANCE (%)														
WH	134	110	1	12.2	26.9	10.2	3.9	-56	-33	0	9	21	58	139
IT	97	83	1	15.6	17.6	10.3	3.6	-42	-7	3	15	27	38	93
PS	90	69	1	11.6	12.6	9.2	3.0	-27	-11	3	11	18	32	41
VA	84	49	1	8.1	19.1	7.3	4.2	-81	-32	1	8	17	25	56
IL	100	69	1	9.1	17.8	9.9	3.4	-58	-37	2	10	16	33	52
BR	69	58	1	7.3	14.5	7.5	3.1	-43	-19	-1	6	15	31	35
LE	72	56	1	11.1	14.7	6.1	4.1	-12	-6	2	8	15	31	79
OX	98	64	1	10.6	13.8	8.4	2.8	-28	-7	2	8	17	32	50
OR	60	59	1	13.0	22.3	12.4	2.8	-95	-60	7	14	20	39	81
CONDUCTIVITY BALANCE (%)														
WH	134	110	1	5.6	33.9	15.6	3.5	-70	-53	-15	-4	25	57	139
IT	97	83	1	28.4	157.7	17.1	3.8	-75	-32	-16	3	22	64	1308
PS	90	69	1	12.7	39.4	16.7	3.3	-36	-33	-15	2	29	72	194
VA	84	49	1	32.4	130.8	16.9	3.4	-35	-35	-11	-2	22	80	827
IL	100	69	1	21.8	88.4	17.6	2.7	-43	-28	-10	7	27	59	695
BR	69	58	1	11.7	39.8	15.1	3.1	-67	-48	-13	3	24	80	144
LE	72	56	1	-0.1	52.3	11.5	3.1	-53	-52	-19	-8	4	37	359
OX	98	64	1	1.0	26.8	13.8	2.8	-53	-28	-18	-5	14	43	105
OR	60	59	1	6.3	34.3	13.7	3.2	-70	-37	-16	0	23	58	171
LAB-FIELD pH														
WH	134	110	1	0.16	0.26	0.11	2.62	-0.29	-0.04	0.05	0.09	0.17	0.65	1.50
IT	97	83	1	0.13	0.23	0.09	2.36	-0.10	0.00	0.05	0.09	0.14	0.26	2.10
PS	90	69	1	0.10	0.06	0.08	2.11	-0.01	0.02	0.05	0.10	0.14	0.20	0.30
VA	84	49	1	0.10	0.14	0.10	1.96	-0.62	-0.07	0.06	0.09	0.14	0.30	0.40
IL	100	69	1	0.06	0.26	0.09	2.88	-1.12	-0.83	0.03	0.07	0.11	0.42	0.60
BR	69	58	1	0.12	0.28	0.09	2.70	-0.34	-0.24	0.03	0.08	0.13	0.28	1.90
LE	72	56	1	0.16	0.15	0.15	1.79	-0.21	-0.18	0.09	0.13	0.20	0.30	0.90
OX	98	64	1	0.08	0.12	0.06	2.76	-0.24	-0.08	0.02	0.08	0.10	0.24	0.80
OR	60	59	1	0.10	0.25	0.07	2.94	-0.35	-0.28	0.02	0.07	0.12	0.24	1.80

TABLE 2.1. (contd)

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centiles					MAX
									5	25	MED	75	95	
ION BALANCE (%)														
pH BIAS PERIOD REMOVED														
WH	134	57	1	10.2	20.6	7.8	4.2	-50	-40	-1	7	18	44	75
IT	97	43	1	13.4	17.2	8.1	4.1	-42	-7	2	7	29	36	52
PS	90	42	1	10.1	12.0	7.3	3.4	-27	-6	2	8	17	27	39
VA	84	27	1	6.2	21.7	6.5	4.8	-81	-81	-1	6	17	24	45
IL	100	42	1	10.5	18.4	9.1	4.2	-58	-37	2	10	19	32	52
BR	69	32	1	4.4	11.4	5.5	3.0	-19	-19	-1	3	9	21	34
LE	72	34	1	7.1	10.2	4.1	4.5	-12	-12	0	5	8	21	44
OX	98	31	1	9.8	17.1	9.0	3.0	-28	-28	-3	7	18	43	44
OR	60	34	1	8.1	24.2	11.1	3.0	-95	-95	6	11	18	26	39
LAB-FIELD pH														
pH BIAS PERIOD REMOVED														
WH	134	57	1	0.10	0.09	0.08	1.99	-0.04	-0.01	0.06	0.08	0.11	0.18	0.60
IT	97	43	1	0.08	0.08	0.06	2.30	-0.10	-0.02	0.03	0.06	0.12	0.20	0.30
PS	90	42	1	0.09	0.05	0.08	2.10	0.01	0.02	0.05	0.10	0.13	0.15	0.20
VA	84	27	1	0.07	0.16	0.09	2.09	-0.62	-0.62	0.04	0.08	0.12	0.17	0.30
IL	100	42	1	0.03	0.20	0.07	2.41	-1.12	-0.28	0.01	0.05	0.09	0.15	0.20
BR	69	32	1	0.04	0.12	0.06	2.63	-0.34	-0.34	0.00	0.04	0.09	0.13	0.40
LE	72	34	1	0.13	0.13	0.14	1.60	-0.21	-0.21	0.09	0.13	0.17	0.24	0.60
OX	98	31	1	0.03	0.07	0.04	2.61	-0.24	-0.24	-0.01	0.04	0.08	0.10	0.10
OR	60	34	1	0.04	0.13	0.05	2.97	-0.35	-0.35	0.01	0.04	0.08	0.24	0.30

TABLE 2.2. Quality Control Measure Statistics for 1987

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centiles					MAX
									5	25	MED	75	95	
ION BALANCE (%)														
WH	111	83	1	5.2	13.8	6.4	3.6	-51	-14	-3	5	11	24	47
IT	101	86	1	8.1	16.5	8.9	2.9	-80	-18	2	9	16	29	44
PS	78	52	1	8.6	8.8	5.7	3.6	-8	-6	1	8	15	21	32
VA	71	51	1	4.8	10.5	5.3	2.7	-22	-20	-2	4	9	26	33
IL	117	74	1	3.9	20.8	7.9	3.3	-77	-30	-5	4	11	28	85
BR	68	58	1	4.1	10.7	6.4	2.8	-18	-17	-3	5	10	22	30
LE	71	56	1	3.6	12.8	5.4	3.2	-57	-29	0	5	8	20	34
OX	114	47	1	3.7	12.6	6.1	3.7	-38	-27	-2	5	11	17	33
OR	63	61	1	4.0	16.5	5.7	3.0	-74	-10	-3	4	8	20	76
CONDUCTIVITY BALANCE (%)														
WH	111	83	1	5.5	20.7	9.6	3.3	-36	-28	-10	3	16	45	85
IT	101	86	1	10.8	21.5	7.6	4.0	-30	-13	-2	6	16	47	115
PS	78	52	1	3.4	23.4	10.6	3.8	-58	-34	-11	-4	20	40	56
VA	71	51	1	6.8	19.8	12.7	2.5	-39	-29	-9	9	16	41	53
IL	117	74	1	2.7	21.9	10.9	2.9	-40	-31	-13	-2	17	33	85
BR	68	58	1	9.8	22.7	11.9	2.9	-29	-25	-7	9	25	44	101
LE	71	56	1	7.2	18.3	10.7	2.7	-30	-21	-7	5	18	41	52
OX	114	47	1	14.0	18.2	11.5	2.9	-21	-18	2	12	22	35	66
OR	63	61	1	10.3	30.7	11.1	3.1	-32	-21	-8	4	21	42	165
LAB-FIELD pH														
WH	111	83	1	0.12	0.12	0.09	2.25	-0.09	0.01	0.05	0.09	0.13	0.23	0.60
IT	101	86	1	0.10	0.04	0.09	1.69	0.00	0.02	0.07	0.09	0.13	0.16	0.20
PS	78	52	1	0.13	0.13	0.11	2.03	-0.19	0.01	0.06	0.12	0.15	0.21	0.90
VA	71	51	1	0.16	0.15	0.11	2.45	-0.01	-0.01	0.06	0.12	0.18	0.37	0.70
IL	117	74	1	0.14	0.13	0.13	2.06	-0.42	-0.12	0.07	0.13	0.18	0.37	0.60
BR	68	58	1	0.11	0.21	0.09	2.20	-0.33	-0.05	0.05	0.08	0.11	0.28	1.40
LE	71	56	1	0.17	0.14	0.15	2.05	-0.38	0.03	0.09	0.14	0.27	0.38	0.50
OX	114	47	1	0.10	0.08	0.09	2.00	-0.11	-0.04	0.05	0.09	0.12	0.22	0.40
OR	63	61	1	0.06	0.11	0.06	2.23	-0.50	-0.03	0.03	0.05	0.08	0.14	0.60

TABLE 2.3. Quality Control Measure Statistics for 1977 Through 1987

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centiles					MAX
									5	25	MED	75	95	
ION BALANCE (%)														
WH	1104	839	11	5.1	21.0	8.0	3.5	-93	-24	-4	4	13	35	139
IT	865	712	11	5.5	16.0	7.6	3.3	-80	-18	-3	5	14	31	97
PS	999	684	11	3.8	15.2	8.2	2.8	-68	-20	-5	4	13	26	67
VA	722	483	11	3.4	15.7	7.0	3.2	-81	-22	-5	3	11	29	72
IL	902	536	10	3.8	16.7	7.9	3.3	-77	-27	-4	4	13	28	85
BR	666	527	9	3.7	14.9	6.8	3.1	-55	-17	-4	3	10	25	108
LE	623	496	9	2.5	15.0	6.3	3.3	-63	-22	-4	3	9	23	79
OX	827	549	9	4.5	14.4	7.0	3.0	-78	-17	-3	4	11	26	75
OR	445	424	7	7.1	16.1	7.6	3.2	-95	-14	0	7	15	29	81
CONDUCTIVITY BALANCE (%)														
WH	1104	839	11	-1.0	19.3	6.9	3.4	-70	-24	-10	-2	6	30	157
IT	865	712	11	4.8	66.0	6.3	4.0	-75	-23	-8	0	7	30	1308
PS	999	684	11	0.1	18.4	6.6	3.5	-58	-22	-9	-2	5	31	194
VA	722	483	11	2.7	44.5	7.0	3.3	-51	-24	-8	-1	8	29	827
IL	902	536	10	0.5	35.0	6.7	3.5	-73	-22	-11	-3	4	30	695
BR	666	527	9	1.5	26.2	6.7	3.6	-67	-23	-10	-1	6	34	352
LE	623	496	9	0.4	21.5	6.6	3.1	-69	-22	-8	-1	7	22	359
OX	827	549	9	1.2	33.4	6.9	3.2	-53	-20	-9	-3	5	27	669
OR	445	424	7	-0.8	19.8	6.0	3.5	-70	-22	-9	-3	3	29	171
LAB-FIELD pH														
WH	1104	839	11	0.13	0.21	0.11	2.70	-0.49	-0.12	0.01	0.09	0.20	0.47	1.50
IT	865	712	11	0.05	0.12	0.05	2.44	-0.86	-0.07	0.00	0.04	0.09	0.19	2.10
PS	999	684	11	0.02	0.26	0.08	2.85	-2.89	-0.25	-0.08	0.01	0.10	0.26	2.30
VA	722	483	11	0.08	0.14	0.07	2.62	-0.62	-0.08	0.01	0.06	0.12	0.30	0.90
IL	902	536	10	0.05	0.19	0.08	2.82	-1.12	-0.16	-0.02	0.05	0.12	0.29	1.40
BR	666	527	9	0.12	0.25	0.08	2.80	-1.40	-0.05	0.03	0.08	0.14	0.38	2.00
LE	623	496	9	0.09	0.18	0.09	2.60	-0.85	-0.12	0.01	0.09	0.15	0.34	1.10
OX	827	549	9	0.12	0.31	0.14	2.99	-2.55	-0.32	0.00	0.09	0.24	0.60	1.80
OR	445	424	7	0.06	0.14	0.06	2.57	-0.50	-0.10	0.00	0.05	0.10	0.25	1.80

TABLE 2.3. (contd)

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centiles					MAX
									5	25	MED	75	95	
ION BALANCE (%)														
pH BIAS PERIOD REMOVED														
WH	1104	761	11	3.4	18.7	7.3	3.5	-93	-24	-4	3	12	29	92
IT	865	651	11	4.2	15.4	7.2	3.3	-80	-18	-4	4	12	29	97
PS	999	646	11	3.1	15.1	8.0	2.8	-68	-20	-6	4	12	24	67
VA	722	455	11	2.9	15.4	6.9	3.2	-81	-22	-5	2	10	29	62
IL	902	490	10	3.3	16.6	7.6	3.4	-77	-27	-4	4	12	27	85
BR	666	486	9	3.3	14.5	6.6	3.1	-55	-16	-5	2	10	24	108
LE	623	467	9	1.7	14.4	6.1	3.3	-63	-22	-5	2	8	22	71
OX	827	501	9	3.8	14.3	6.8	3.0	-78	-17	-4	4	10	24	75
OR	445	390	7	6.2	15.7	7.2	3.1	-95	-16	-1	6	14	28	76
LAB-FIELD pH														
pH BIAS PERIOD REMOVED														
WH	1104	761	11	0.12	0.19	0.10	2.67	-0.49	-0.12	0.00	0.08	0.20	0.46	1.30
IT	865	651	11	0.04	0.10	0.05	2.39	-0.86	-0.08	-0.01	0.04	0.08	0.17	0.90
PS	999	646	11	0.01	0.27	0.08	2.87	-2.89	-0.25	-0.09	0.01	0.09	0.26	2.30
VA	722	455	11	0.08	0.14	0.07	2.64	-0.62	-0.08	0.01	0.06	0.12	0.30	0.90
IL	902	490	10	0.05	0.18	0.07	2.81	-1.12	-0.16	-0.02	0.04	0.11	0.27	1.40
BR	666	486	9	0.11	0.25	0.08	2.81	-1.40	-0.07	0.02	0.08	0.14	0.37	2.00
LE	623	467	9	0.09	0.18	0.09	2.60	-0.85	-0.12	0.01	0.09	0.15	0.34	1.10
OX	827	501	9	0.12	0.32	0.14	3.03	-2.55	-0.33	-0.01	0.09	0.25	0.60	1.80
OR	445	390	7	0.06	0.12	0.06	2.54	-0.50	-0.10	-0.01	0.05	0.10	0.25	0.70

2.3 LABORATORY QUALITY CONTROL

Accuracy is a measure of the difference between a known-concentration value and the value obtained from an analytical measurement. Since the measured value is often the mean of a number of determinations, accuracy can include precision, or the degree of agreement of repeated measurements. Bias is the measure of a systematic positive or negative difference between known and measured values. Our definition of accuracy A (%) for a series of measurements on the same known solution is

$$A = \frac{\text{Mean}(|K - M|)}{\text{Mean}(K)} \times 100 \quad (2.4)$$

where K is the known value and M is the measured value. Bias B (%) is the same, except that the actual difference is used:

$$B = \frac{\text{Mean}(K - M)}{\text{Mean}(K)} \times 100 . \quad (2.5)$$

Precision P (%) is defined as the coefficient of variation (standard deviation/mean) of a series of concentration measurements of the same solution. The concentration need not be known, since repeatability is the only consideration.

The known-concentration samples used for calculation of the variables are the QC standard solutions. The QA plan requires the analysis, once for every 10 samples analyzed, of a known-concentration sample. This sample is prepared from calibration standard solutions, but is not used in calibration. Results for QC standard runs during 1986 and 1987 are summarized in Table 2.4 and Figure 2.1. The two parameters (sulfur-IV and conductivity) for which more than one QC solution was used are listed separately in the lower portion of the table; the values given for precision in the species-summary (upper) portion of the table are simply the highest among the several known values. The nominal goals for acceptability of all three variables are listed (as "estimated error") in Table 1.3. All of the species met these goals; however, the concentrations of potassium and sodium in the QC solutions were in the

TABLE 2.4. Laboratory Quality Control Summary for 1986 and 1987

Species No.	Species	N	K	M	Prec	Accu	Bias
15	S(IV) (a)	102			8.39	0.06	-0.02
16	SO4--	228	32.4	31.8	3.32	2.58	1.75
18	NO3-	225	30.6	30.3	4.71	3.59	0.93
19	Cl-	209	15.9	16.1	8.66	6.77	-1.60
13	H+	111	40.7	40.5	2.77	1.90	0.50
14	COND. (a)	104			8.11	5.10	1.29
22	NH4+	142	20.8	21.0	6.01	4.87	-1.18
23	Na+	85	217.0	215.0	3.15	2.20	1.02
24	K+	86	127.0	129.0	10.20	8.28	-1.28
26	Ca++	82	25.0	24.8	2.86	1.96	0.72
27	Mg++	84	41.0	40.9	3.39	1.94	0.23
15	S(IV)	47	3.2	3.2	8.39	0.07	-0.01
15	S(IV)	55	15.9	16.2	7.04	0.06	-0.02
14	COND.	58	18.0	18.0	8.11	6.13	-0.19
14	COND.	23	20.0	19.6	3.64	3.04	2.17
14	COND.	23	22.0	21.1	4.62	4.54	4.15

(a) Precision for S(IV) and COND is taken as highest of the values obtained for the several known concentrations or conductivities. Accuracy and bias are weighted means.

N = Number of sample runs

K = Known concentration value (μM) or conductivity ($\mu\text{mho/cm}$)

M = Average measured concentration value (μM) or conductivity ($\mu\text{mho/cm}$)

Prec = Precision (%)

Accu = Accuracy (%)

Bias = Bias (%)

upper range of expected sample concentrations, and chloride was marginal in terms of frequency of meeting the goal in individual sample runs. Additional QC assessment work is under way that will probably lead to the setting of more conservative analytical goals for these species, or a change of method in the case of potassium.

Accuracy, bias, and precision evaluations using the USGS blind sample analysis program are discussed in Section 4.

FIGURE 2.1. Accuracy, Bias, and Precision Estimates for Chemical Analyses from 1986-1987 QC Check Sample Data

FIGURE 2.1. Accuracy, Bias, and Precision Estimates for Chemicals
Analyses from 1999-1997 DC Check data.

3.0 DATA SUMMARY FOR 1986, 1987, AND 1977 THROUGH 1987

3.1 INTRODUCTION

Laboratory and field data that have been accepted after quality assessments are incorporated into a data base that is used for calculation of statistical summaries and for special data applications. In addition, PCN data are communicated to the data base facility at Brookhaven National Laboratory and to the Atmospheric Deposition System (ADS) (Watson and Olsen 1984), maintained by PNL for the U.S. Environmental Protection Agency. These are the data sources for readers interested in conducting their own analyses. The statistical summaries and other analyses presented in this section use methods the same as those and formats similar to those presented in the 1985 report (Dana 1988) or summary articles (MAP3S/RAINE Research Community 1982; Dana and Easter 1987); thus, minimal descriptive detail is given here.

Statistical calculations require that the data base be edited to remove samples with missing chemistry or precipitation data, or to remove samples with low collection efficiency. The editing procedure is presented in Appendix C. Summaries of results for single species contain an edited number of samples; this number will not necessarily be the same (or contain the identical group of samples) as that for another species. Calculations of precipitation statistics may employ different data bases depending on whether the precipitation is that accompanying a selected chemical species, or whether it is selected as a species.

3.2 EDITING STATISTICS

Table 3.1 lists the numbers of samples removed from sea-salt-corrected sulfur (SSCS) general statistics (distribution) calculations for the individual years 1986 and 1987 and for the period 1977 through 1987. Since sulfate is a major ion (nearly always above detection limit) and has primary priority for analysis, it shows the least number of samples removed for low volume (ISA) or being below the minimum detection limit (MDL). Other species, with lower priority, higher detection limit, or lower concentration values, will have

TABLE 3.1. Editing Statistics for Sea-Salt-Corrected Sulfur Distribution Calculations

SITE	N	NEDT	YRS	Numbers of Events Removed								PFR
				VOL	CE	MSG	MDL	ISA	NAP	MOE	RPC	
1986												
WH	134	113	1	3	6	12	0	12	0	0	0	0.972
IT	97	92	1	0	4	1	0	1	0	0	0	0.975
PS	90	78	1	1	6	5	0	5	0	0	0	0.976
VA	84	55	1	2	3	24	0	23	0	0	1	0.948
IL	100	73	1	1	6	20	0	20	0	0	0	0.988
BR	69	59	1	3	1	6	0	6	0	0	0	0.997
LE	72	57	1	1	1	13	0	13	0	0	0	0.993
OX	98	72	1	3	5	18	0	18	0	0	0	0.995
OR	60	60	1	0	0	0	0	0	0	0	0	1.000
ALL	804	659	1	14	32	99	0	98	0	0	1	0.983
1987												
WH	111	84	1	4	5	18	0	17	0	0	1	0.919
IT	101	91	1	0	7	3	0	2	0	0	1	0.980
PS	78	67	1	1	3	7	0	7	0	0	0	0.954
VA	71	53	1	0	0	18	0	17	0	0	1	1.000
IL	117	75	1	4	3	35	0	35	0	0	0	0.979
BR	68	61	1	1	1	5	0	5	0	0	0	0.990
LE	71	58	1	0	1	12	0	12	0	0	0	0.983
OX	114	80	1	2	12	20	0	20	0	0	0	0.983
OR	63	62	1	0	1	0	0	0	0	0	0	0.988
ALL	794	631	1	12	33	118	0	115	0	0	3	0.975
1977-1987												
WH	1104	936	11	19	28	121	0	101	2	11	7	0.972
IT	865	790	11	3	46	26	0	17	2	3	4	0.957
PS	999	860	11	17	33	89	0	79	0	5	5	0.980
VA	722	553	11	19	51	99	0	91	0	4	4	0.920
IL	902	581	10	14	84	223	0	206	3	11	3	0.875
BR	666	545	9	8	33	80	0	70	0	3	7	0.971
LE	623	513	9	3	20	87	0	86	0	1	0	0.947
OX	827	616	9	7	51	153	1	143	0	5	4	0.967
OR	445	435	7	0	5	5	0	2	0	0	3	0.984
ALL	7153	5829		90	351	883	1	795	7	43	37	0.944

N	Total no. of events	MDL	Species conc. below MDL
NEDT	No. of events after edit	ISA	Insufficient sample for analysis
YRS	Years in record analyzed	NAP	No analysis performed
VOL	Precip. missing	MOE	Malfunction or operator error
CE	Collection effic. below 0.5	RPC	Probable contamination
MSG	Missing analysis	PFR	Frac. of precip. in remaining events

fewer samples included in statistical summaries. The numbers of samples removed for reasons of low collection efficiency, missing precipitation amount, and contamination are not species-specific.

The history of editing statistics illustrates the degree of consistency of both field and laboratory procedures. Figure 3.1 shows the average number of samples per site by year. The early increase was due to a combination of the addition of new sites, which tended to collect more samples, and an improvement in procedures whereby small-volume samples were more accurately accounted for. Figure 3.2 shows the fractions of SSCS samples for the entire network that are removed for various causes. The increase in missing values early in the network history parallels the change in total reported samples--that is, many of the additional samples had missing values, mainly because of insufficient volume for chemical analysis. The reason for the decrease in collection efficiency losses is less clear; it probably is associated with better precipitation data collection and better laboratory and field attention paid to calculated and measured volumes. The largest proportion of the missing values for SSCS (and other major species) is due to low sample volume.

One of the minor species, sodium, has a greater number of both ISA and MDL samples. Editing statistics for sodium are shown in Table 3.2, and Figure 3.3 compares missing values for SSCS and sodium. The increase for sodium in recent years reflects the change of analysis method to ICAP, which requires larger volumes for analysis. At the same time, the number of MDL samples also increased, although the detection limit for the ICAP method is about the same as that for the former IC method. Factors contributing to an increase in the number of MDL samples include ICAP operator judgement, an unrealistically low assignment of detection limit for the ICAP method, and an increased emphasis on accurate determination of the sodium values from the coastal sites, which are at times much higher than those for the other sites. Despite the large percentage of samples removed from the minor-species data bases, the fraction of precipitation removed is relatively small.

FIGURE 3.1. Mean Number of Samples Per Site Per Year

FIGURE 3.2. Percent of Samples Removed from Total Network Statistics Data Base Because of Missing Rainfall, Low Collection Efficiency, and Missing Chemical Results

TABLE 3.2 Editing Statistics for Sodium Distribution Calculations

SITE	N	NEDT	YRS	Numbers of Events Removed								PFR
				VOL	CE	MSG	MDL	ISA	NAP	MOE	RPC	
1986												
WH	134	59	1	3	6	66	53	13	0	0	0	0.972
IT	97	64	1	0	4	29	21	8	0	0	0	0.975
PS	90	53	1	1	6	30	16	14	0	0	0	0.976
VA	84	46	1	2	3	33	4	28	0	0	1	0.948
IL	100	63	1	1	6	30	7	23	0	0	0	0.988
BR	69	58	1	3	1	7	0	7	0	0	0	0.997
LE	72	55	1	1	1	15	1	14	0	0	0	0.993
OX	98	50	1	3	5	40	17	23	0	0	0	0.995
OR	60	55	1	0	0	5	4	1	0	0	0	1.000
ALL	804	503	1	14	32	255	123	131	0	0	1	0.983
1987												
WH	111	50	1	4	5	52	33	17	0	0	2	0.919
IT	101	66	1	0	7	28	22	5	0	0	1	0.980
PS	78	51	1	1	3	23	14	9	0	0	0	0.954
VA	71	43	1	0	0	28	9	18	0	0	1	1.000
IL	117	65	1	4	3	45	10	35	0	0	0	0.979
BR	68	59	1	1	1	7	1	6	0	0	0	0.990
LE	71	57	1	0	1	13	0	12	0	0	1	0.983
OX	114	68	1	2	12	32	9	23	0	0	0	0.983
OR	63	53	1	0	1	9	8	1	0	0	0	0.988
ALL	794	512	1	12	33	237	106	126	0	0	5	0.975
1977-1987												
WH	1020	698	11	19	26	277	151	106	2	11	7	0.971
IT	810	633	11	1	39	137	98	31	2	3	3	0.964
PS	905	687	11	15	29	174	63	101	1	5	4	0.984
VA	671	468	11	19	48	136	27	100	0	4	5	0.939
IL	902	541	10	14	84	263	36	210	3	11	3	0.875
BR	666	540	9	8	33	85	1	73	2	3	6	0.971
LE	623	509	9	3	20	91	1	87	0	2	1	0.947
OX	827	556	9	7	51	213	44	159	0	5	5	0.967
OR	445	407	7	0	5	33	21	8	1	0	3	0.984
ALL	6869	5039		86	335	1409	442	875	11	44	37	0.950

N Total no. of events
 NEDT No. of events after edit
 YRS Years in record analyzed
 VOL Precip. missing
 CE Collection effic. below 0.5
 MSG Missing analysis

MDL Species conc. below MDL
 ISA Insufficient sample for analysis
 NAP No analysis performed
 MOE Malfunction or operator error
 RPC Probable contamination
 PFR Frac. of precip. in remaining events

FIGURE 3.3. Comparison of Missing Chemistry Values for Sodium and Sulfate: Total Network Statistics Data Base

3.3 DISTRIBUTION AND PRECIPITATION-WEIGHTED STATISTICS

Tables 3.3 through 3.5b list distribution statistics for individual years 1986 and 1987, the period 1977 through 1987 (whole years), and for the accumulated seasons, December 1976 through November 1986. Listed are the major ionic species [sulfate, SSCS, nitrate, chloride, and hydrogen (from laboratory pH), ammonium and sodium] and the precipitation amount. Chloride and sodium are included since they are major species for the coastal sites Brookhaven and Lewes. The pH bias period (January 1 through June 30) (Dana 1988) is not included in the hydrogen statistics for 1986 or in those for the cumulative data base. Only SSCS is tabulated for the seasons.

TABLE 3.3. Distribution Statistics for 1986

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centiles					MAX
									5	25	MED	75	95	
S (μM)														
WH	134	113	1	28	28	18	2.6	1	3	11	19	33	79	180
IT	97	92	1	38	34	27	2.4	3	5	15	29	49	96	219
PS	90	78	1	46	35	34	2.3	5	6	16	37	63	100	150
VA	84	55	1	43	38	33	2.1	6	7	21	32	41	110	201
IL	100	73	1	43	42	33	1.9	10	15	22	27	43	117	290
BR	69	59	1	35	29	24	2.5	1	4	12	26	44	90	129
LE	72	57	1	37	27	28	2.1	6	6	15	29	49	77	155
OX	98	72	1	35	19	30	1.8	5	9	22	28	46	64	104
OR	60	60	1	37	27	30	1.9	9	11	19	28	42	91	150
SSCS (μM)														
WH	134	113	1	28	28	18	2.6	1	3	11	19	33	79	180
IT	97	92	1	38	34	27	2.4	3	5	15	29	49	96	219
PS	90	78	1	46	35	34	2.3	5	6	16	37	62	100	150
VA	84	55	1	43	38	32	2.2	5	7	21	32	41	110	201
IL	100	73	1	43	42	33	1.9	10	15	21	27	43	117	290
BR	69	59	1	33	29	22	2.7	1	4	9	24	44	87	129
LE	72	57	1	34	27	25	2.4	4	4	14	28	48	76	154
OX	98	72	1	34	19	30	1.8	5	9	22	28	46	64	102
OR	60	60	1	36	27	29	1.9	9	11	18	28	41	90	150
NO ₃ (μM)														
WH	134	112	1	30	32	20	2.6	*	5	11	19	36	86	230
IT	97	91	1	45	42	35	2.0	7	11	22	36	55	89	363
PS	90	78	1	52	32	41	2.1	7	9	25	47	73	98	150
VA	84	55	1	45	35	35	2.1	6	7	21	36	57	90	208
IL	100	73	1	41	38	30	2.2	8	10	16	26	57	97	200
BR	69	59	1	42	37	27	2.8	2	3	12	27	61	125	140
LE	72	57	1	35	27	24	2.7	2	3	13	30	51	84	106
OX	98	71	1	33	20	27	2.0	3	8	16	27	42	67	104
OR	60	60	1	30	23	23	2.0	6	7	14	24	36	71	124

TABLE 3.3. (contd)

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centiles					MAX
									5	25	MED	75	95	
Cl (μM)														
WH	134	113	1	12	68	4	2.8	*	*	3	4	7	15	723
IT	97	92	1	9	6	7	1.9	*	3	5	7	10	18	38
PS	90	78	1	11	8	9	1.8	2	3	6	9	14	22	41
VA	84	55	1	10	5	9	1.7	3	3	6	9	12	18	29
IL	100	73	1	10	6	8	1.8	2	3	6	8	10	20	37
BR	69	59	1	36	42	24	2.4	5	6	12	22	42	105	245
LE	72	57	1	50	63	29	2.7	4	6	14	24	50	143	341
OX	98	72	1	8	6	6	1.9	1	2	4	6	9	15	40
OR	60	60	1	10	5	9	1.7	2	4	6	9	12	19	30
H (μM) (from laboratory pH)														
WH	134	60	1	49	33	40	1.9	8	12	26	36	62	118	141
IT	97	47	1	73	61	55	2.1	14	15	30	48	91	162	316
PS	90	43	1	103	72	81	2.1	17	20	43	87	148	219	288
VA	84	29	1	82	55	67	1.9	16	16	45	66	91	166	240
IL	100	43	1	65	46	54	1.8	14	21	34	50	69	148	214
BR	69	32	1	67	63	43	2.7	5	5	21	42	81	195	219
LE	72	34	1	72	61	48	2.8	5	5	23	55	93	186	269
OX	98	36	1	64	45	53	1.8	11	11	39	50	71	115	263
OR	60	34	1	80	70	60	2.1	20	20	34	51	83	246	309
NH ₄ (μM)														
WH	134	113	1	20	23	10	4.0	*	*	5	12	26	66	104
IT	97	89	1	25	28	15	3.0	1	2	7	18	33	58	204
PS	90	76	1	23	18	16	2.5	2	2	9	17	29	52	86
VA	84	55	1	31	49	20	2.6	2	3	9	24	34	57	360
IL	100	73	1	40	59	24	2.6	4	5	12	22	37	113	350
BR	69	59	1	18	18	11	3.1	*	*	6	13	21	45	100
LE	72	57	1	21	21	13	2.9	*	2	7	13	23	56	120
OX	98	72	1	25	21	18	2.4	2	3	10	17	33	71	93
OR	60	60	1	18	19	13	2.5	*	3	7	13	22	56	118

TABLE 3.3. (contd)

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centiles					MAX
									5	25	MED	75	95	
Na (μ M)														
WH	134	112	1	1.3	2.8	0.6	2.9	*	*	*	0.5	1.2	3.5	19.0
IT	97	85	1	2.0	2.5	1.0	3.1	*	*	*	0.9	2.2	7.5	12.0
PS	90	69	1	2.4	4.7	1.2	3.1	*	*	*	1.3	2.5	5.5	38.0
VA	84	50	1	3.6	4.7	2.0	3.1	*	*	0.8	2.1	4.2	8.5	23.0
IL	100	70	1	3.2	3.3	2.0	2.9	*	*	1.0	2.4	4.0	7.8	18.0
BR	69	58	1	26.1	32.3	14.9	2.9	0.8	1.6	6.8	13.9	29.0	82.9	168.0
LE	72	56	1	35.6	50.8	15.4	4.2	*	0.7	6.4	14.5	41.5	110.0	273.0
OX	98	67	1	2.6	5.2	1.2	3.4	*	*	*	1.0	2.6	7.1	40.0
OR	60	59	1	4.0	4.7	2.3	3.0	*	*	0.9	2.1	5.4	13.0	27.0

Precipitation (cm)

WH	134	125	1	1.00	1.00	0.55	3.66	0.00	0.03	0.25	0.61	1.44	2.81	5.30
IT	97	93	1	1.17	1.18	0.67	3.35	0.03	0.05	0.31	0.77	1.55	3.28	6.40
PS	90	83	1	1.26	1.43	0.55	4.64	0.01	0.03	0.16	0.75	1.83	4.06	6.30
VA	84	79	1	1.03	1.32	0.34	6.47	0.00	0.01	0.09	0.42	1.39	3.75	5.50
IL	100	93	1	0.96	1.48	0.26	7.25	0.00	0.00	0.08	0.36	0.81	4.84	7.00
BR	69	65	1	1.67	1.69	0.90	3.60	0.04	0.07	0.42	1.02	2.34	4.84	7.10
LE	72	70	1	1.31	1.41	0.69	3.71	0.02	0.08	0.28	0.77	1.92	3.28	7.80
OX	98	90	1	1.14	1.31	0.40	6.71	0.00	0.01	0.15	0.58	1.56	4.06	4.70
OR	60	60	1	1.82	1.88	1.09	2.97	0.08	0.18	0.47	1.14	2.02	5.70	8.30

LEGEND:

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

TABLE 3.4. Distribution Statistics for 1987

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centiles					MAX
									5	25	MED	75	95	
S (μM)														
WH	111	84	1	20	16	14	2.4	1	3	8	17	26	52	68
IT	101	91	1	41	47	27	2.5	2	5	15	28	53	102	385
PS	78	67	1	46	41	32	2.5	3	5	18	37	59	100	252
VA	71	53	1	28	26	19	2.5	2	2	11	21	31	61	152
IL	117	75	1	34	25	24	2.9	0	1	14	25	47	73	147
BR	68	61	1	34	32	24	2.4	2	5	11	24	43	86	196
LE	71	58	1	35	41	23	2.3	6	6	14	21	41	81	270
OX	114	80	1	39	31	31	1.9	6	10	19	29	45	102	190
OR	63	62	1	35	31	28	1.9	4	10	20	29	38	63	230
SSCS (μM)														
WH	111	84	1	20	16	14	2.4	1	3	8	16	26	52	67
IT	101	91	1	40	47	27	2.5	2	5	15	28	52	102	385
PS	78	67	1	46	41	31	2.5	3	5	18	36	59	99	252
VA	71	53	1	27	26	19	2.5	2	2	11	21	31	61	152
IL	117	75	1	33	25	23	3.0	0	1	14	25	47	73	147
BR	68	61	1	32	32	21	2.6	2	4	9	22	41	86	196
LE	71	58	1	32	42	19	2.7	3	3	8	16	40	77	269
OX	114	80	1	38	31	31	1.9	6	10	19	29	44	101	190
OR	63	62	1	35	31	27	2.0	4	10	20	29	38	63	230
NO3 (μM)														
WH	111	84	1	28	23	20	2.3	3	5	11	18	37	74	101
IT	101	91	1	55	50	40	2.2	7	10	23	39	70	128	310
PS	78	67	1	53	59	39	2.1	9	11	22	38	61	98	465
VA	71	53	1	34	31	25	2.2	5	6	15	22	37	93	149
IL	117	75	1	37	35	26	2.8	0	1	19	25	44	92	245
BR	68	61	1	45	47	27	3.0	2	4	12	34	57	110	224
LE	71	58	1	40	44	25	2.7	3	5	11	28	51	118	244
OX	114	80	1	36	23	30	1.8	8	10	19	32	49	67	164
OR	63	62	1	31	20	25	2.0	5	6	16	27	35	66	93

TABLE 3.4. (contd)

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centiles					MAX
									5	25	MED	75	95	
Cl (μM)														
WH	111	84	1	7	5	4	3.2	*	*	4	6	9	14	29
IT	101	91	1	10	7	8	1.8	2	2	6	9	11	20	41
PS	78	67	1	11	7	9	1.9	*	4	7	10	13	19	43
VA	71	53	1	10	14	7	2.7	*	*	4	6	10	24	96
IL	117	75	1	9	4	8	1.6	2	3	5	8	11	20	22
BR	68	61	1	32	25	24	2.1	3	8	13	24	39	75	140
LE	71	58	1	52	53	33	2.6	6	7	16	29	51	150	204
OX	114	80	1	9	5	7	2.2	*	2	6	8	10	18	27
OR	63	62	1	9	5	8	1.7	3	3	5	9	11	16	26
H (μM) (from laboratory pH)														
WH	111	83	1	40	28	30	2.3	3	8	17	32	55	93	112
IT	101	92	1	83	102	59	2.2	7	13	35	63	100	174	912
PS	78	68	1	87	67	63	2.5	2	9	37	63	118	195	347
VA	71	53	1	58	57	43	2.2	5	10	26	40	68	123	380
IL	117	75	1	46	32	32	2.8	1	3	22	40	62	98	141
BR	68	61	1	73	59	52	2.5	6	11	26	56	98	166	288
LE	71	58	1	67	79	43	2.6	7	8	18	46	87	219	490
OX	114	78	1	64	42	51	2.0	7	12	32	53	81	135	195
OR	63	62	1	64	48	52	2.0	6	15	36	50	76	126	316
NH ₄ (μM)														
WH	111	83	1	18	16	11	3.4	*	*	6	16	26	44	92
IT	101	90	1	28	28	19	2.6	1	3	11	22	34	79	190
PS	78	68	1	33	62	20	2.5	2	4	12	21	31	64	511
VA	71	53	1	20	16	13	2.6	1	2	6	16	23	54	69
IL	117	76	1	34	37	18	3.8	*	*	10	24	41	103	223
BR	68	61	1	23	38	12	3.0	1	2	5	12	27	51	281
LE	71	58	1	22	22	13	3.0	1	2	5	13	30	59	115
OX	114	80	1	31	30	22	2.6	*	4	13	23	43	70	227
OR	63	62	1	20	17	13	3.3	*	*	10	16	24	41	85

TABLE 3.4. (contd)

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centiles					MAX
									5	25	MED	75	95	
Na (μ M)														
WH	111	83	1	1	3	1	2.5	*	*	*	1	1	3	26
IT	101	88	1	2	4	1	3.2	*	*	*	1	3	7	31
PS	78	65	1	2	2	1	2.9	*	*	*	1	2	6	12
VA	71	52	1	6	14	2	4.3	*	*	1	1	3	17	90
IL	117	75	1	4	5	2	3.3	*	*	1	2	4	17	22
BR	68	60	1	23	24	13	3.4	*	1	5	16	29	69	127
LE	71	57	1	43	64	19	3.6	2	2	8	17	36	148	355
OX	114	77	1	2	4	1	2.9	*	*	1	1	2	7	22
OR	63	61	1	3	3	2	3.0	*	*	1	2	3	7	16

Precipitation (cm)

WH	111	102	1	0.97	1.06	0.50	3.7	0.01	0.05	0.19	0.64	1.25	3.13	5.60
IT	101	94	1	1.01	1.04	0.55	3.6	0.01	0.06	0.23	0.59	1.45	3.13	5.20
PS	78	74	1	1.22	1.32	0.52	5.9	0.00	0.01	0.22	0.72	1.88	3.75	6.90
VA	71	71	1	2.16	3.64	0.65	6.4	0.01	0.02	0.16	0.89	2.50	7.66	23.40
IL	117	110	1	0.84	1.50	0.17	9.4	0.00	0.00	0.05	0.20	0.86	3.59	11.10
BR	68	66	1	1.61	1.68	0.85	3.7	0.05	0.05	0.31	1.13	2.34	4.38	8.30
LE	71	70	1	1.38	1.52	0.59	4.5	0.03	0.05	0.15	0.50	2.03	4.06	5.90
OX	114	100	1	0.74	0.96	0.30	5.0	0.00	0.01	0.10	0.38	1.16	2.66	5.60
OR	63	62	1	1.55	1.71	0.93	2.9	0.07	0.19	0.42	0.91	2.03	5.63	7.00

LEGEND:

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

TABLE 3.5. Distribution Statistics for 1977 Through 1987

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centiles					MAX
									5	25	MED	75	95	
S (μM)														
WH	1104	936	11	27	25	19	2.4	1	4	11	21	35	75	243
IT	865	790	11	39	37	28	2.3	1	6	16	29	49	100	385
PS	999	860	11	45	38	32	2.4	2	7	18	36	60	110	340
VA	722	553	11	37	33	27	2.3	2	7	16	27	45	100	250
IL	902	581	10	40	31	31	2.0	0	11	21	31	48	87	290
BR	666	545	9	34	30	24	2.4	1	6	13	24	44	96	196
LE	623	513	9	31	27	23	2.2	2	6	14	23	41	75	270
OX	827	617	9	37	25	30	1.9	2	10	20	30	47	82	190
OR	445	435	7	36	29	29	1.9	4	10	19	30	44	84	250
SSCS (μM)														
WH	1104	936	11	27	25	19	2.4	1	4	11	21	35	74	240
IT	865	790	11	39	37	28	2.4	1	6	16	29	49	100	385
PS	999	860	11	44	37	32	2.4	2	7	18	35	60	110	340
VA	722	553	11	36	33	26	2.3	2	6	16	27	45	100	245
IL	902	581	10	39	31	31	2.1	0	11	21	31	48	87	290
BR	666	545	9	32	30	21	2.6	0	4	10	22	42	95	196
LE	623	513	9	28	27	19	2.6	1	4	10	20	40	74	269
OX	827	617	9	37	25	30	2.0	2	10	20	29	46	81	190
OR	445	435	7	36	29	29	1.9	4	10	19	29	44	83	250
NO3 (μM)														
WH	1104	936	11	31	28	22	2.3	*	6	13	24	41	85	260
IT	865	790	11	45	38	35	2.1	3	11	21	35	56	110	363
PS	999	860	11	51	39	39	2.1	2	11	25	41	64	124	465
VA	722	553	11	37	37	27	2.1	3	8	17	27	43	90	530
IL	902	581	10	40	31	31	2.1	0	11	19	31	50	100	245
BR	666	546	9	40	42	24	3.0	*	4	11	26	55	129	280
LE	623	513	9	32	33	20	2.8	*	3	10	23	42	91	320
OX	827	615	9	34	22	28	1.9	3	9	18	28	45	74	164
OR	445	435	7	29	21	23	2.0	2	7	14	23	36	70	130

TABLE 3.5. (contd)

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centiles					MAX
									5	25	MED	75	95	
C1 (μM)														
WH	1104	935	11	6	24	4	2.7	*	*	2	4	6	15	723
IT	865	791	11	8	9	6	2.4	*	2	4	6	9	20	140
PS	999	856	11	10	9	7	2.5	*	2	5	8	12	28	84
VA	722	545	11	11	25	7	2.4	*	2	4	7	12	28	460
IL	902	583	10	8	7	6	2.0	*	2	4	6	10	19	79
BR	666	547	9	37	45	23	2.5	2	5	12	22	44	110	540
LE	623	514	9	57	84	32	2.9	1	7	14	30	68	170	1200
OX	827	616	9	7	6	6	2.0	*	2	4	6	9	18	73
OR	445	435	7	9	6	7	1.9	1	3	5	7	11	20	51
H (μM) (from laboratory pH)														
WH	1104	844	11	56	42	43	2.2	1	11	26	46	74	130	372
IT	865	712	11	85	69	66	2.1	2	20	43	69	105	195	912
PS	999	758	11	93	66	71	2.4	0	18	48	78	120	230	479
VA	722	510	11	76	67	58	2.1	5	17	35	59	91	200	850
IL	902	549	10	61	53	40	3.2	0	3	30	49	78	151	603
BR	666	517	9	72	65	46	2.9	0	8	23	52	100	204	370
LE	623	484	9	61	56	40	2.7	0	7	21	46	83	159	490
OX	827	571	9	66	44	53	2.2	0	16	36	55	83	151	309
OR	445	398	7	66	51	53	2.0	2	18	36	54	81	162	398
NH4 (μM)														
WH	1104	924	11	19	21	10	3.5	*	1	5	12	24	59	164
IT	865	783	11	24	25	14	3.0	*	2	8	17	31	64	216
PS	999	840	11	24	30	15	2.9	*	2	8	17	30	66	511
VA	722	548	11	21	26	13	3.1	*	2	7	15	28	57	360
IL	902	581	10	32	36	21	2.6	*	5	12	23	39	87	350
BR	666	546	9	19	25	10	3.6	*	1	4	12	25	61	281
LE	623	514	9	18	18	11	3.2	*	1	5	11	27	56	120
OX	827	614	9	24	23	17	2.6	*	3	10	18	31	67	227
OR	445	434	7	16	15	10	3.1	*	1	6	12	22	41	118

TABLE 3.5. (contd)

SITE	N	NEDT	YRS	AME	ASD	GME	GSD	MIN	Centiles					MAX
									5	25	MED	75	95	
Na (μM)														
WH	1020	849	10	3	5	1	3.1	*	*	1	1	3	9	51
IT	810	731	10	3	5	2	3.1	*	*	1	2	3	11	66
PS	905	750	10	5	6	2	3.3	*	*	1	2	5	18	47
VA	671	495	10	7	21	3	3.5	*	*	1	3	6	22	390
IL	902	577	10	4	6	2	3.0	*	*	1	2	5	15	78
BR	666	541	9	31	39	17	3.1	*	3	8	17	39	98	450
LE	623	510	9	47	68	23	3.6	*	3	10	23	60	150	890
OX	827	600	9	4	5	2	3.0	*	*	1	2	5	14	40
OR	445	428	7	6	8	3	3.1	*	*	1	3	7	18	57
Precipitation (cm)														
WH	1104	1057	11	1.15	1.34	0.61	3.6	0.00	0.05	0.27	0.74	1.50	3.67	12.90
IT	865	816	11	1.35	1.39	0.78	3.3	0.01	0.08	0.38	0.91	1.83	4.29	9.20
PS	999	949	11	1.23	1.45	0.53	4.7	0.00	0.03	0.20	0.71	1.74	4.38	10.60
VA	722	652	11	1.74	2.32	0.71	4.9	0.00	0.03	0.29	0.90	2.34	5.71	23.40
IL	902	804	10	0.99	1.47	0.27	7.7	0.00	0.00	0.08	0.40	1.27	3.84	12.70
BR	666	625	9	1.62	1.82	0.81	3.8	0.01	0.08	0.33	0.92	2.27	5.00	12.10
LE	623	600	9	1.59	1.96	0.75	4.1	0.01	0.05	0.30	0.94	2.24	4.80	20.90
OX	827	769	9	1.12	1.38	0.48	4.6	0.00	0.03	0.18	0.59	1.56	4.04	11.10
OR	445	440	7	1.89	1.97	1.10	3.1	0.02	0.16	0.48	1.22	2.57	6.20	14.60

LEGEND:

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

TABLE 3.5b. Distribution Statistics for SSCS (μM) for Accumulated Seasons (all available, December 1976 through November 1986)

<u>SITE</u>	<u>N</u>	<u>NEDT</u>	<u>AME</u>	<u>ASD</u>	<u>GME</u>	<u>GSD</u>	<u>MIN</u>	<u>MED</u>	<u>MAX</u>
Spring (March-May)									
WH	263	232	29	23	22	2.20	2.3	24	169
IT	187	171	43	38	32	2.17	1.7	34	263
PS	216	190	43	34	34	1.99	3.3	35	280
VA	170	132	36	31	27	2.05	5.5	26	201
IL	237	152	43	35	35	1.85	6.8	32	290
BR	186	147	37	35	27	2.26	3.6	27	187
LE	136	121	27	19	21	2.09	3.8	22	92
OX	208	161	35	18	32	1.65	5.4	31	102
OR	98	95	34	18	29	1.71	7.0	30	109
Summer (June-August)									
WH	284	243	38	32	29	2.19	1.9	29	240
IT	209	200	57	43	46	1.93	7.3	45	315
PS	252	215	65	39	54	1.97	2.2	57	340
VA	206	158	51	37	41	1.98	6.8	40	224
IL	209	143	49	36	40	1.89	3.6	37	280
BR	169	128	42	32	30	2.50	1.2	34	144
LE	175	140	43	32	32	2.39	1.9	37	157
OX	190	151	53	30	46	1.70	11.9	47	179
OR	113	108	51	41	40	1.99	8.1	40	250
Autumn (September-November)									
WH	242	213	24	21	18	2.27	1.8	20	189
IT	193	180	33	24	25	2.20	0.7	27	139
PS	218	193	44	38	32	2.32	2.9	34	328
VA	136	103	36	35	26	2.26	4.1	24	245
IL	190	129	35	25	30	1.77	9.5	27	189
BR	148	125	28	26	18	2.84	0.4	20	126
LE	135	112	23	20	16	2.37	1.6	16	88
OX	158	119	29	18	25	1.79	5.0	25	109
OR	81	81	32	21	26	1.89	5.9	27	114

TABLE 3.5b. (contd)

<u>SITE</u>	<u>N</u>	<u>NEDT</u>	<u>AME</u>	<u>ASD</u>	<u>GME</u>	<u>GSD</u>	<u>MIN</u>	<u>MED</u>	<u>MAX</u>
Winter (December-February)									
WH	195	158	15	14	11	2.22	1.3	11	109
IT	170	144	17	15	13	2.00	1.8	14	155
PS	239	199	22	20	16	2.25	1.9	16	147
VA	131	101	20	15	15	2.08	2.7	16	84
IL	147	82	26	17	22	1.90	2.4	22	97
BR	137	111	19	19	13	2.38	1.3	12	112
LE	146	116	17	13	12	2.47	0.7	12	55
OX	156	104	22	15	18	2.10	1.7	20	119
OR	76	75	24	13	21	1.77	4.1	22	60
All Months (1977-1986)									
WH	993	852	28	26	20	2.37	1.3	22	240
IT	764	699	39	36	28	2.34	0.7	29	315
PS	921	793	44	37	31	2.39	1.9	35	340
VA	651	500	37	33	27	2.24	2.7	27	245
IL	785	506	40	31	32	1.91	2.4	31	290
BR	598	484	32	30	21	2.63	0.4	22	187
LE	552	455	28	24	19	2.54	0.7	20	157
OX	713	537	36	24	29	1.96	1.7	29	179
OR	382	373	36	28	29	1.93	4.1	29	250

LEGEND:

N	Total number of events
NEDT	Number of events after edit
AME	Arithmetic mean
ASD	Arithmetic standard deviation
GME	Geometrical mean
GSD	Geometrical standard deviation
MIN	Minimum value
MED	Median (50th percentile)
MAX	Maximum value

Precipitation-weighted average concentrations (WA) are calculated using

$$WA = \frac{\sum_{j=1}^N c_j p_j}{\sum_{j=1}^N p_j}$$

where c_j and p_j are concentration and precipitation amounts for event (or daily) sample j , respectively, and N is the total number of samples, after editing, in the period of interest. The monthly weighted averages (MWA) for major species are listed in Tables 3.6 and 3.7, along with average precipitation per sample, and total precipitation for the periods. Blanks in the tables represent entries where less than 50% of the precipitation of the period had usable chemistry. For hydrogen ion from laboratory pH, the entire first half of 1986, during which the pH measurement bias occurred, is blank. Two sites had less than 50% of their yearly precipitation with valid pH measurements and are shown as blanks in Table 3.6. Table 3.8 lists the corresponding accumulated monthly weighted averages (AMWA), where monthly data from all available years are combined. Annual weighted averages are listed in Table 3.9.

3.4 TEMPORAL TRENDS

Temporal trends for logarithms of concentrations of the major ions were examined by Dana and Easter (1987), using the data base for 1977 through 1983. The parameters from the regression analyses differed little whether one used event (daily) data or MWA. Table 3.10 shows results of updated calculations for $\log[\text{SSCS}]$ and calculations for SSCS, using 1976 through 1987 MWA. The results compare closely to those reported by Dana and Easter for all but the coastal sites. It appears that the trends for the older sites are quite stable, with little difference between those through 1983 and those through 1987. The data bases for the younger sites have, of course, become more robust, and the trends at these sites are similar to those for the older sites.

TABLE 3.6. Monthly Weighted Averages (MWA) for 1986

SITE	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YEAR
SSCS (μM)													
WH	4	17	24	22	23	27	27	26	30	16	9	12	22
IT	8	17	29	38	33	36	24	48	47	28	10	10	27
PS	10	26	20	36	21	60	51	71	45	30	15	15	33
VA	16	37	11		43	37	44	27	41	23	21	15	30
IL		18	25	53	39	30	30	30	25	23	21	22	28
BR	12	32	18	46	25	39	29	17	57	18	12	9	20
LE	8	32	23	51	10	40	36	28	41	12	18	9	23
OX	25	23	24	38	52	35	30	35	12	29	17	16	27
OR	20	21	26	34	33	43	21	35	35	10	20	25	25
NO ₃ (μM)													
WH	10	31	35	22	24	20	22	17	18	15	17	18	20
IT	23	42	42	41	25	25	22	30	39	29	18	24	29
PS	27	58	22	48	24	42	41	37	35	28	20	22	33
VA	21	65	16		37	26	30	25	39	45	19	46	35
IL		30	20	56	30	22	27	22	15	21	17	18	23
BR	24	51	20	39	34	40	30	17	68	23	13	11	23
LE	9	44	24	50	13	30	33	26	33	7	20	9	23
OX	38	27	18	28	39	25	22	23	7	19	17	18	22
OR	26	16	21	25	24	25	16	24	26	9	15	21	19
NH ₄ (μM)													
WH	3	8	22	24	22	20	25	14	10	9	7	6	15
IT	5	11	18	24	30	23	13	21	56	16	6	6	19
PS	3	18	13	27	13	24	15	34	16	12	12	11	16
VA	6	32	12		28	23	25	16	23	24	14	15	21
IL		21	29	93	30	14	18	15	11	17	13	8	19
BR	6	21	8	29	18	24	13	7	19	7	7	4	10
LE	4	19	17	40	9	32	20	16	14	10	12	5	15
OX	24	19	23	30	53	21	12	19	4	17	9	8	19
OR	13	12	18	26	20	24	9	20	11	4	7	10	13

TABLE 3.6. (contd)

SITE	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YEAR
H (μ M)													
WH							49	59	48	37	23	29	44
IT							52	82	91	53	28	24	
PS							119	148	86	69	37	40	76
VA							84	63	92	80	47	35	64
IL							53	56	56	46	34	38	50
BR							70	40	143	42	25	19	40
LE							75	60	103	18	41	20	46
OX							61	75	24	49	34	36	
OR							39	61	67	27	51	51	48

Average Precipitation Per Event (cm)

WH	1.17	0.71	0.84	0.49	1.00	1.27	1.17	1.14	1.32	0.70	1.14	0.61	0.98
IT	1.69	0.99	0.97	1.19	1.56	1.28	1.68	0.98	0.65	0.83	1.14	1.23	1.15
PS	0.54	1.09	1.68	1.84	1.19	1.32	1.46	0.56	0.81	1.04	2.33	1.45	1.20
VA	1.00	0.84	0.82	0.57	0.64	0.57	1.41	1.30	1.17	1.25	1.01	2.89	1.05
IL	0.05	0.71	0.27	0.34	1.23	3.61	1.26	0.39	1.48	0.74	0.56	0.53	0.91
BR	0.98	0.93	1.62	0.74	0.93	0.96	3.40	1.98	0.48	1.98	2.65	3.30	1.66
LE	2.34	1.11	1.61	1.22	0.81	1.25	1.30	1.38	0.29	1.30	0.92	2.89	1.30
OX	0.75	1.11	1.04	0.71	1.25	1.10	1.22	0.60	1.57	1.45	0.93	1.08	1.08
OR	1.70	2.21	1.37	0.81	2.58	0.93	3.80	1.44	1.22	3.11	1.59	2.64	1.82

Precipitation Per Period (cm)

WH	9.4	5.0	10.9	4.4	13.0	15.2	11.7	16.0	17.1	7.7	11.4	6.7	128.5
IT	8.5	7.9	7.8	9.5	9.4	15.3	15.1	6.8	6.5	8.3	9.1	7.4	111.6
PS	5.4	9.8	8.4	7.4	8.3	10.6	13.1	3.9	8.1	8.4	16.3	7.2	107.0
VA	3.0	6.7	4.1	5.7	4.5	4.6	12.7	13.0	5.9	5.0	9.1	11.6	85.7
IL	0.1	5.7	2.1	2.7	9.8	18.1	10.1	3.1	19.2	8.2	6.7	4.2	90.1
BR	5.9	6.5	8.1	5.9	2.8	3.9	13.6	15.8	2.4	5.9	18.5	19.8	109.2
LE	11.7	9.9	3.2	6.1	3.2	5.0	10.4	12.4	1.7	5.2	9.2	14.4	92.5
OX	3.7	12.2	10.4	5.7	10.0	9.9	10.9	3.6	12.6	8.7	8.4	6.5	102.7
OR	5.1	13.3	6.8	4.1	7.7	3.7	11.4	11.5	8.6	12.4	11.1	13.2	109.0

TABLE 3.7. Monthly Weighted Averages (MWA) for 1987

SITE	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YEAR
SSCS (μM)													
WH	8	18	10	15		33	33	16	11	8	21	11	18
IT	9	14	15	15	63	42	32	38	31	18	18	12	26
PS	8	17	17	26	46	60	48	43	45	21	9	14	34
VA	6	7	22	16	33	27	18	64	12	26	11	24	18
IL		12	33	33	41	33	35	38	36	23	15	15	29
BR	8	18	10	12	48	31	47	33	28	14	19	15	20
LE	9	10	8	7	26	41	59	94	15	9	14	19	22
OX	32		20	27	57	33	28	81	30	21	18	23	31
OR	13	23	19	21	24	37	35	65	34	26	15	25	26
NO₃ (μM)													
WH	17	66	17	19		18	20	11	11	15	46	24	21
IT	32	98	26	21	53	40	25	34	35	32	28	23	32
PS	20	68	39	32	44	46	36	30	43	32	16	25	35
VA	17	23	32	25	39	19	23	32	11	34	15	29	20
IL		11	40	41	39	29	23	29	22	28	14	14	25
BR	9	56	12	12	64	38	45	25	36	14	22	23	24
LE	14	9	15	10	32	33	46	79	16	11	18	33	24
OX	37		22	34	45	24	20	56	22	24	19	19	27
OR	13	25	15	25	26	30	15	39	17	26	13	15	20
NH₄ (μM)													
WH	7	29	8	11		24	26	10	9	8	22	10	16
IT	8	20	9	13	55	28	21	17	16	18	27	9	19
PS	6	20	17	19	28	64	16	23	27	17	6	10	24
VA	4	5	19	13	32	20	14	23	9	25	10	16	13
IL		6	46	46	43	21	23	37	31	26	7	7	24
BR	2	17	4	5	40	15	25	19	24	12	11	8	12
LE	4	4	8	5	21	35	44	58	15	6	11	15	16
OX	28		13	24	38	22	16	49	25	29	9	11	21
OR	5	7	11	21	30	14	14	33	17	18	9	15	14

TABLE 3.7. (contd)

SITE	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YEAR
H (μ M)													
WH	25	67	22	31		58	54	28	23	24	58	33	37
IT	36	70	29	29	88	74	56	91	73	46	37	35	54
PS	25	62	47	53	89	91	98	88	102	57	21	37	70
VA	22	27	50	33	60	52	41	105	26	44	26	58	37
IL		19	39	33	52	51	54	58	49	43	28	33	45
BR	19	63	24	23	99	75	97	68	69	32	40	36	45
LE	23	18	19	15	52	77	100	185	32	20	30	53	45
OX	68		40	46	95	55	49	137	58	48	40	39	56
OR	23	54	34	34	39	77	60	115	64	55	32	45	49

Average Precipitation Per Event (cm)

WH	0.89	0.45	1.00	1.02	0.93	1.11	1.14	1.37	1.07	1.19	1.12	0.72	1.01
IT	0.92	0.38	0.88	1.48	0.53	0.72	1.30	1.60	0.92	1.22	0.49	0.98	0.96
PS	1.51	0.64	0.94	2.02	1.64	1.48	0.65	2.40	0.93	0.79	1.09	0.99	1.23
VA	2.02	1.05	1.30	6.20	1.04	1.99	0.25	0.89	5.46	1.12	4.49	1.20	2.16
IL	0.26	0.21	0.42	0.61	0.58	1.19	1.78	0.83	0.64	0.47	0.96	1.13	0.84
BR	3.06	1.09	1.73	3.31	0.69	0.92	0.75	2.33	1.21	1.21	1.78	1.69	1.60
LE	2.92	1.93	1.39	2.13	1.26	0.60	0.92	1.41	0.67	1.63	1.91	0.93	1.39
OX	0.27	0.28	1.17	0.64	0.83	0.67	1.75	0.34	0.15	0.35	0.64	0.64	0.68
OR	1.83	1.73	1.63	1.38	1.21	1.75	2.91	0.54	1.95	0.55	1.92	1.68	1.55

Precipitation Per Period (cm)

WH	8.0	3.1	6.0	7.1	8.3	8.9	14.8	11.0	12.8	9.5	11.2	7.2	108.0
IT	9.2	2.3	4.4	13.3	4.8	6.5	15.6	9.6	9.2	9.8	4.5	7.9	97.1
PS	4.5	2.5	3.7	16.2	8.2	10.4	6.5	14.4	8.4	5.6	6.6	7.9	94.8
VA	12.1	4.2	9.1	24.8	6.2	15.9	2.3	5.3	49.2	4.5	13.5	6.0	153.1
IL	2.9	1.0	3.4	7.3	4.1	10.7	24.9	10.0	4.5	2.8	11.5	11.3	94.4
BR	15.3	4.4	6.9	19.8	4.1	5.5	5.3	11.6	9.6	7.3	5.3	11.8	107.1
LE	17.5	5.8	8.3	12.8	7.6	5.4	7.3	5.7	3.3	9.8	7.6	7.4	98.6
OX	2.4	0.8	9.4	7.7	7.5	5.4	19.2	3.8	1.2	3.2	7.0	8.3	75.8
OR	12.8	6.9	13.1	8.3	6.0	10.5	8.7	3.2	11.7	2.2	5.8	8.4	97.6

TABLE 3.8. Accumulated Monthly Weighted Averages (AMWA)
for 1977 Through 1987

SITE	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YEAR
SSCS (μM)													
WH	8	14	16	23	27	31	27	34	20	18	13	11	21
IT	11	17	19	28	35	44	42	50	34	24	16	13	29
PS	12	18	22	32	35	48	54	55	40	25	16	17	32
VA	11	16	18	24	29	35	35	43	23	19	18	15	25
IL	21	22	29	32	30	35	38	36	32	25	20	18	29
BR	11	15	18	17	28	23	35	29	35	16	11	13	20
LE	11	15	14	20	25	36	38	30	24	15	13	12	21
OX	18	25	27	31	37	35	41	52	22	25	20	18	30
OR	22	22	24	22	27	36	34	36	33	19	21	18	26
NO ₃ (μM)													
WH	24	29	25	25	23	23	19	21	15	18	20	21	21
IT	28	41	30	31	32	32	28	32	28	27	22	26	30
PS	26	34	29	36	33	35	36	35	34	27	22	27	31
VA	17	23	21	25	26	25	25	28	17	22	22	23	23
IL	25	25	29	33	26	27	27	26	22	22	18	20	25
BR	12	20	19	16	28	21	32	27	34	18	13	16	21
LE	15	20	15	20	23	31	31	22	20	16	17	16	20
OX	23	27	27	29	25	26	28	33	17	21	18	17	24
OR	18	16	17	17	21	26	22	23	21	13	15	14	18
NH ₄ (μM)													
WH	7	8	11	16	20	19	18	16	11	10	9	8	13
IT	8	9	12	18	23	25	19	23	19	15	9	8	16
PS	6	10	14	19	23	25	27	24	21	14	8	8	17
VA	4	9	11	16	20	21	17	20	13	12	10	8	14
IL	11	14	23	32	23	21	22	22	21	22	16	9	20
BR	3	7	9	9	21	14	19	15	19	10	6	6	11
LE	5	8	9	15	18	23	23	16	14	11	8	7	13
OX	10	15	20	24	27	22	20	25	12	17	11	11	18
OR	7	6	12	13	23	17	13	15	15	7	7	7	12

TABLE 3.8. (contd)

SITE	JAN	FEB	MAR	APR	MAY	JUN	JUL	AUG	SEP	OCT	NOV	DEC	YEAR
H (μ M)													
WH	37	47	41	46	45	60	50	65	40	40	37	34	46
IT	40	59	47	61	71	86	85	97	72	56	46	40	66
PS	41	51	56	69	69	91	107	112	80	58	42	50	71
VA	38	42	44	48	56	69	67	85	45	47	48	43	54
IL	46	51	55	43	44	54	65	60	55	43	36	43	51
BR	23	32	41	32	50	49	73	70	75	36	27	32	44
LE	30	33	31	35	48	67	74	60	49	32	39	33	45
OX	46	57	55	53	51	57	80	94	41	55	42	42	57
OR	44	46	43	36	37	63	59	68	60	40	45	43	49

Average Precipitation Per Event (cm)

WH	0.83	0.88	0.92	1.01	1.19	1.09	1.08	1.29	1.46	1.45	1.38	1.11	1.15
IT	1.32	1.19	1.32	1.36	1.26	1.38	1.44	1.37	1.48	1.36	1.34	1.14	1.33
PS	0.92	1.07	1.28	1.26	1.59	1.35	1.20	1.31	1.17	1.15	1.37	0.88	1.21
VA	1.84	1.75	1.58	2.03	1.68	1.33	1.52	1.56	2.38	1.78	1.98	1.66	1.73
IL	0.48	0.73	0.76	0.81	1.14	1.11	1.52	1.63	0.90	0.86	1.10	0.85	1.02
BR	1.94	1.63	1.47	1.93	1.16	1.72	1.30	1.55	1.26	1.53	1.96	1.55	1.58
LE	1.71	1.30	2.14	1.91	1.96	1.45	1.30	2.01	1.53	1.68	1.66	1.39	1.66
OX	0.58	1.04	1.11	1.02	1.36	1.01	1.32	0.90	0.83	1.20	1.49	1.05	1.09
OR	1.62	2.23	1.71	1.78	2.05	1.41	1.96	1.63	1.82	2.21	2.30	2.34	1.90

Average Precipitation Per Period (cm)

WH	5.4	5.4	7.6	9.2	9.8	10.1	9.2	12.8	13.4	10.8	10.8	9.1	113.6
IT	8.2	6.2	8.2	9.4	7.2	10.6	9.7	9.6	9.5	9.3	9.0	7.7	104.5
PS	6.8	7.0	8.9	9.2	10.7	12.2	9.5	9.8	7.9	8.5	10.2	7.5	108.1
VA	7.7	8.6	8.9	10.9	9.3	7.4	11.0	11.4	11.1	8.4	8.1	7.9	110.6
IL	2.2	3.5	6.3	6.9	7.8	8.3	11.4	11.7	5.4	5.3	8.1	5.7	82.7
BR	8.3	7.1	9.2	11.6	6.7	10.2	7.0	8.9	5.9	7.4	10.5	9.0	101.7
LE	7.9	7.1	10.3	9.0	8.7	7.9	7.9	12.4	6.3	8.0	7.9	7.1	100.5
OX	3.0	5.1	7.1	7.4	10.4	6.7	9.3	5.7	4.2	7.3	9.5	7.2	82.9
OR	5.2	7.1	6.2	6.0	7.5	5.5	7.1	6.7	5.1	6.2	6.7	7.7	76.9

TABLE 3.9. Annual Weighted Averages

SPECIES	YR	Site								
		WH	IT	PS	VA	IL	BR	LE	OX	OR
SSCS (μM)										
	77	22	29	35	36					
	78	28	34	31	28	34				
	79	20	27	24	23		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	27
	86	21	27	33	30	28	20	23	27	25
	87	18	25	34	18	29	20	22	31	26
NO ₃ (μM)										
	77	23	29	31	30					
	78	25	32	31	24	28				
	79	20	25	24	18		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
	86	20	29	33	35	23	23	23	22	19
	87	21	32	35	20	25	24	24	27	20
NH ₄ (μM)										
	77	11	13	15	16					
	78	17	16	14	12	24				
	79	11	15	14	10		11	12	19	
	80	17	17	16	17	22	18	15	25	
	81	12	17	25	16	22	12	16	20	13
	82	11	15	20	15	19	8	10	16	9
	83	11	16	13	13	15	7	12	16	8
	84	14	14	17	11	22	9	12	17	14
	85	13	19	19	13	18	15	12	16	12
	86	15	19	16	21	19	10	15	19	13
	87	15	19	24	13	24	12	16	21	14

TABLE 3.9. (contd)

SPECIES	YR	Site								
		WH	IT	PS	VA	IL	BR	LE	OX	OR
H (μ M)										
	77	47	70	77	71					
	78	59	85	79	67					
	79	50	69	59	62		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	48	63	73	48	51	55	37	56	54
	86	44		75	64	50	40	46		48
	87	37	54	70	37	45	45	45	56	49
Precipitation (cm)										
	77	125	107	122	71					
	78	86	86	97	109	64				
	79	112	112	137	134	80	111	143	95	
	80	96	97	88	87	92	84	96	99	
	81	123	123	104	91	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
	86	129	112	107	86	90	109	93	103	109
	87	108	97	95	153	94	107	99	76	98

TABLE 3.10. Trend Statistics for SSCS: 1977 Through 1987

SITE	YR	YRS	Linear(a)				Periodic(b)					
			A	B	PST	R ₂	α	β	γ	ϕ	RSP	R ₂
WH	77	11	1.33	-0.010	-1.98	0.017	1.33	-0.010	0.24	1.63	1.16	0.53
IT	77	11	1.46	-0.010	-1.99	0.015	1.47	-0.011	0.30	1.71	1.47	0.68
PS	77	11	1.44	0.001	0.16	0.000	1.47	-0.003	0.30	1.78	1.51	0.67
VA	77	11	1.49	-0.017	-3.24	0.050	1.47	-0.016	0.23	1.80	1.12	0.51
IL	78	10	1.52	-0.010	-2.04	0.035	1.52	-0.009	0.14	1.66	0.66	0.45
BR	79	9	1.33	-0.002	-0.51	0.001	1.32	-0.001	0.23	1.69	1.10	0.39
LE	79	9	1.31	-0.004	-0.94	0.002	1.31	-0.005	0.26	1.62	1.27	0.45
OX	79	9	1.52	-0.010	-2.09	0.022	1.53	-0.011	0.18	1.60	0.83	0.49
OR	81	7	1.47	-0.006	-1.40	0.006	1.48	-0.007	0.15	1.72	0.68	0.38

SITE	YR	YRS	Linear(c)				Periodic(d)					
			A	B	PST	R ₂	α	β	γ	ϕ	RSP	R ₂
WH	77	11	24.73	-0.544	-2.20	0.025	25.01	-0.570	10.96	1.672	0.89	0.50
IT	77	11	35.40	-0.871	-2.46	0.021	35.74	-0.934	19.16	1.734	1.09	0.53
PS	77	11	32.80	0.065	0.20	0.000	34.92	-0.209	22.22	1.846	1.28	0.50
VA	77	11	35.36	-1.173	-3.32	0.053	34.74	-1.132	14.27	1.865	0.84	0.45
IL	78	10	33.99	-0.549	-1.62	0.024	33.51	-0.515	8.89	1.688	0.53	0.39
BR	79	9	25.55	-0.178	-0.70	0.011	25.18	-0.143	11.17	1.754	0.89	0.28
LE	79	9	21.25	0.243	1.14	0.002	21.31	0.216	13.63	1.679	1.27	0.42
OX	79	9	34.77	-0.549	-1.58	0.012	35.53	-0.667	12.42	1.677	0.71	0.43
OR	81	7	30.71	-0.319	-1.04	0.003	31.53	-0.414	9.93	1.816	0.63	0.38

$$(a) \log(C) = A + BT$$

$$(b) \log(C) = \alpha + \beta T + \gamma \sin(2\pi t - \phi)$$

$$(c) C = A + BT$$

$$(d) C = \alpha + \beta T + \gamma \sin(2\pi t - \phi)$$

LEGEND:

YRS	Years of record
PST	Percent change per year (average over yrs)
R ₂	R-squared for regression
RSP	Ratio of amplitude to mean
T	Years since January 1, 1976

It is interesting to note that Penn State and Lewes are the only sites to not show a downward trend. The contrasts in linear slopes and the amplitudes of the periodic (annual) trends are illustrated in Figures 3.4 through 3.12, which show SSCS MWA for the 9 sites. The concentration trends are slightly less significant statistically than those for the logarithms, but they are more meaningful graphically. The only trends in SSCS MWA that are statistically significant at the $p < 0.05$ level (Student's-t test) are those for Ithaca and Virginia.

FIGURE 3.4. Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Whiteface. R-squared values for the regressions are 0.02 and 0.50, respectively.

FIGURE 3.5. Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Ithaca. R-squared values for the regressions are 0.02 and 0.53, respectively.

FIGURE 3.6. Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Penn State. R-squared values for the regressions are 0.00 and 0.49, respectively.

FIGURE 3.7. Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Virginia. R-squared values for the regressions are 0.05 and 0.44, respectively.

FIGURE 3.8. Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Illinois. R-squared values for the regressions are 0.02 and 0.39, respectively.

FIGURE 3.9. Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Brookhaven. R-squared values for the regressions are 0.01 and 0.27, respectively.

FIGURE 3.10. Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Lewes. R-squared values for the regressions are 0.00 and 0.41, respectively.

FIGURE 3.11. Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Oxford. R-squared values for the regressions are 0.01 and 0.43, respectively.

FIGURE 3.12. Monthly Weighted Average Data, and Linear and Periodic Concentration Trends for Oak Ridge. R-squared values for the regressions are 0.00 and 0.38, respectively.

4.0 EXTERNAL QUALITY ASSURANCE

External QA for PCN is provided by the U.S. Geological Survey (USGS) (Schroder, Bricker, and Willoughby 1985), which directs site operators to periodically submit blind audit samples to the PCN laboratory. The results of the chemical analyses (which are treated as regular samples because they are assigned fictitious sample identification and field data) are compared with USGS measured values, once the samples have been identified and removed from the PCN data base. During 1986 and 1987, 49 such samples were processed through PCN; these were drawn from 15 different standard USGS audit solutions listed in Table 4.1. The samples are identified by USGS numbers, and, for convenience in preparing this report, a PCN code value (used in the subsequent table). In general, the concentration values for these samples are lower than those included in previous years (Rothert and Dana 1984; Dana 1987, 1988), but well within the normal range of concentration values for regular PCN samples.

TABLE 4.1. External Blind Samples Analyzed During 1986 and 1987, and USGS Most Probable Concentration Values (μM)

USGS Solution #	PCN Code	N(a)	SO ₄	NO ₃	Cl	NH ₄	Na	K	Ca	Mg
0484-1-1:1	1	2	25.4	8.41	8.40	6.38	9.43	1.94	1.34	0.82
0484-1-2:1	2	3	12.7	4.20	4.20	3.22	4.74	0.97	0.67	0.41
0485-1-1:1	3	1	24.1	8.29	10.0	5.72	8.35	2.09	1.54	0.69
0485-1-2:1	4	1	12.0	4.40	5.04	2.88	4.17	1.04	0.77	0.37
1084-1-2:1	5	8	13.5	4.24	4.23	2.94	3.82	0.92	0.97	0.41
1085-3-10:1	7	11	35.2	14.0	23.2	5.44	2.21	13.1	9.23	1.60
1085-3-20:1	8	6	17.6	7.03	11.6	2.72	1.13	6.57	4.74	0.82
M2100:1	9	5	22.0	1.93	9.02	(b)	28.7	0.94	15.4	11.5
M4100:1	10	3	2.08	0.14	0.78	(b)	2.00	0.28	2.84	1.23
M420:1	11	4	10.3	0.67	3.94	(b)	10.0	1.40	14.2	6.16
M425:1	12	2	8.22	0.54	3.15	(b)	8.00	1.12	11.3	4.93
M450:1	13	6	4.16	0.27	1.57	(b)	4.00	0.56	5.68	2.46
M90100:	14	7	12.5	0.17	1.18	(b)	2.56	0.56	6.48	4.23
M9050:1	15	6	25	0.33	2.36	(b)	5.13	1.12	12.9	8.47
NITRATE-2	16	2	15.6	16.1	(b)	(b)	16.1	(b)	(b)	(b)

(a) Number of times analyzed by PCN.

(b) No value reported.

Figures 4.1 through 4.7 compare the USGS "most probable value" with the values obtained by PCN, and Table 4.2 lists summary statistics for the comparisons. Nitrate is not represented in the comparisons because it has been found that it is not well preserved in these samples (Schroder, Bricker, and Willoughby 1985). The standard laboratory quality measures of bias, precision, and accuracy (see Section 2) are calculated, but it should be noted that the latter two are based on the most probable concentrations, rather than very well known concentrations, such as resulting from samples prepared directly from quality-assured standards. In addition, the definition of precision assumes that the repeated analyses are of a single sample, whereas the samples here are separate aliquots, subjected to different handling conditions and aging. The results for most species are near PCN laboratory goals (see Table 1.3), but the comparison is not favorable for chloride and potassium, and two outliers appeared for sulfate. The latter are unexplained, as both samples' results had been analyzed in duplicate, and proper QC checks were

FIGURE 4.1. Comparison of PCL Values and USGS Most Probable Values for Calcium

FIGURE 4.2. Comparison of PCL Values and USGS Most Probable Values for Chloride

FIGURE 4.3. Comparison of PCL Values and USGS Most Probable Values for Magnesium

FIGURE 4.4. Comparison of PCL Values and USGS Most Probable Values for Potassium

FIGURE 4.5. Comparison of PCL Values and USGS Most Probable Values for Sodium

FIGURE 4.6. Comparison of PCL Values and USGS Most Probable Values for Ammonium

FIGURE 4.7. Comparison of PCL Values and USGS Most Probable Values for Sulfate

TABLE 4.2. Summary of External Blind Samples Results

PCN CODE	SPECIES	N(a)	USGS MEAN (μ M)	PCN MEAN (μ M)	PREC (%)	ACCU (%)	BIAS (%)	PCN GOAL(b) (%)
5	SO ₄	8	13.5	13.9	5.6	5.5	-2.5	10
7		11	35.2	32.5	9.6	7.8	7.8	10
8		6	17.6	20.2	31	19	-15	10
9		5	22.1	21.0	15	10	4.9	10
13		6	4.2	4.2	10	8.9	-1.2	10
14		7	12.5	13.6	14	12	-8.6	10
15		6	25.0	25.3	4.4	4.0	-1.3	10
5	Cl	8	4.2	5.7	12	34	-34	47
7		11	23.3	26.5	12	17	-14	10
8		6	11.7	15.3	27	33	-32	17
9		5	9.0	16.4	17	82	-82	22
13		6	1.6	4.7	73	230	-200	127
14		7	1.2	7.2	48	500	-500	169
15		6	2.4	6.4	38	170	-170	84
5	NH ₄	8	2.9	3.0	27	18	-1.0	17
7		11	5.4	10.1	73	103	-85	10
8		6	2.7	3.7	39	55	-35	18
5	Na	8	3.8	2.7	33	30	29	10
7		11	2.2	2.0	19	18	12	18
8		6	1.1	1.3	35	40	-18	35
9		5	28.7	23.4	5.1	18	18	10
13		6	4.0	3.3	12	17	17	10
14		7	2.6	1.9	25	27	27	16
15		6	5.1	4.6	6.8	11	11	10
5	K	8	0.9	1.0	61	54	-3.2	54
7		11	13.1	16.8	28	37	-27	10
8		6	6.6	8.4	66	78	-28	10
9		5	0.9	3.5	78	305	-265	53
13		6	0.6	2.5	120	450	-350	89
14		7	0.6	0.5	160	130	11	89
15		6	1.1	1.8	130	170	-58	44

TABLE 4.2. (contd)

PCN CODE	SPECIES	N(a)	USGS MEAN (μ M)	PCN MEAN (μ M)	PREC (%)	ACCU (%)	BIAS (%)	PCN GOAL(b) (%)
5	Ca	8	1.0	0.8	120	79	14	21
7		11	9.2	9.2	1.8	1.3	-0.06	10
8		6	4.7	5.7	26	34	0.5	10
9		5	15.5	15.8	4.7	4.6	-2.1	10
13		6	5.7	5.7	9.1	7.9	0.09	10
14		7	6.5	6.3	2	2.5	2.4	10
15		6	13.0	12.5	4	3.9	3.7	10
5	Mg	8	0.4	0.2	130	80	45	49
7		11	1.6	1.5	11	8.8	5.7	12
8		6	0.8	0.9	25	31	4.8	24
9		5	11.5	11.2	3.5	4.4	2.8	10
13		6	2.5	2.4	5.6	5.2	2.1	10
14		7	4.2	4.1	4.8	3.4	2.5	10
15		6	8.5	8.3	1.9	2.1	1.7	10

(a) Number of times analyzed by PCN.

(b) See Table 1.3.

favorable. As noted in Section 2, laboratory goals for potassium and chloride are being reevaluated, and a change of analysis method is being considered for potassium (cation chromatography, which would also include ammonium and sodium).

5.0 REFERENCES

- Bigelow, D. S. 1986. Quality Assurance Report, NADP/NTN Deposition Monitoring: Field Operations July 1978 through December 1983. National Atmospheric Deposition Program, Colorado State University, Fort Collins, Colorado.
- Dana, M. Terry. 1987. The MAP3S Precipitation Chemistry Network: Eighth Periodic Summary Report (1984). PNL-6055, Pacific Northwest Laboratory, Richland, Washington.
- Dana, M. Terry. 1988. The MAP3S Precipitation Chemistry Network: Ninth Periodic Summary Report (1985). PNL-6461, Pacific Northwest Laboratory, Richland, Washington.
- Dana, M. Terry, and R. C. Easter. 1987. "Statistical Summary and Analysis of Event Precipitation Chemistry from the MAP3S Network, 1976-1983." Atmos. Environ. 21:113-128.
- Dana, M. Terry, and J. E. Rothert. 1983. The MAP3S Precipitation Chemistry Network: Fifth Periodic Summary Report (January 1981-December 1981). PNL-4599, Pacific Northwest Laboratory, Richland, Washington.
- Dana, M. Terry, and J. E. Rothert. 1984. The MAP3S Precipitation Chemistry Network: Sixth Periodic Summary Report (January 1982-December 1982). PNL-4787, Pacific Northwest Laboratory, Richland, Washington.
- James, K. D. W. 1988. Quality Assurance Report, NADP/NTN Deposition Monitoring: Laboratory Operations, Central Analytical Laboratory, January 1986 Through December 1986. Illinois State Water Survey, Champaign, Illinois.
- MAP3S. 1977. The MAP3S Precipitation Chemistry Network: First Periodic Summary Report (September 1976-June 1977). PNL-2402, Pacific Northwest Laboratory, Richland, Washington.
- MAP3S. 1978. The MAP3S Precipitation Chemistry Network: Second Periodic Summary Report (July 1977-June 1978). PNL-2829, Pacific Northwest Laboratory, Richland, Washington.
- MAP3S. 1980a. The MAP3S/RAINE Precipitation Chemistry Network: Quality Control. PNL-3612, Pacific Northwest Laboratory, Richland, Washington.
- MAP3S. 1980b. The MAP3S Precipitation Chemistry Network: Third Periodic Summary Report (July 1978-December 1979). PNL-3400, Pacific Northwest Laboratory, Richland, Washington.
- MAP3S. 1981. The MAP3S Precipitation Chemistry Network: Fourth Periodic Summary Report (January 1980-December 1980). PNL-4144, Pacific Northwest Laboratory, Richland, Washington.

- MAP3S/RAINE Research Community. 1982. "The MAP3S/RAINE Precipitation Chemistry Network: Statistical Overview for the Period 1976-1979." Atmos. Environ. 16:1603-1631.
- Peden, M. E., et al. 1986. Development of Standard Methods for the Collection and Analysis of Precipitation. Illinois State Water Survey Contract Report 381, Champaign, Illinois.
- Rothert, J. E., and M. Terry Dana. 1984. The MAP3S Precipitation Chemistry Network: Seventh Periodic Summary Report (1983). PNL-5298, Pacific Northwest Laboratory, Richland, Washington.
- Schroder, L. J., A. W. Bricker and T. C. Willoughby. 1985. Precision Bias of Selected Analytes Reported by National Atmospheric Deposition Program and National Trends Network - January 1980 through September 1984. Water Resources Investigations Report No. 85-4275, U.S. Geological Survey, Lakewood, Colorado.
- Watson, C. R., and A. R. Olsen. 1984. Acid Deposition System (ADS) for Statistical Reporting: System Design & Users Code Manual. PNL-4826, Pacific Northwest Laboratory, Richland, Washington.

APPENDIX A

STANDARD OPERATING PROCEDURES

APPENDIX A

STANDARD OPERATING PROCEDURES

MAP3S Precipitation Chemistry Network (MAP3S/PCN) operations at the Pacific Northwest Laboratory (PNL) are divided into two major activities: network management and chemical analysis of precipitation samples. Network management is the responsibility of the Atmospheric Sciences Department and includes site supply, site performance audits, data reporting, and general network management.

The primary function of the Precipitation Chemistry Laboratory (PCL) is chemical analysis of precipitation samples collected by the sites in the MAP3S/PCN. Attendant to this function are sample identification, custody and control, chemical analysis of samples for major ions, and computer data entry and quality control.

Assurance of uniformity of performance of the various tasks associated with the MAP3S/PCN is facilitated through the use of written standard operating procedures, or SOPs. These procedures, which are integral components of the formal QA plan, cover all major laboratory and network management activities, and are designed, along with reference manuals and standards for performance, to be training tools for new personnel. Procedures change continuously as new methods for doing tasks are introduced and as network priorities are modified. Thus, the SOPs are frequently reviewed for current applicability and modified as necessary.

Table A.1 is a list of current SOPs. The main text of this report may reference tables and figures taken from these SOPs. Those SOPs that deal primarily with network management activities have the prefix PCN; those SOPs that deal with chemical analysis tasks in the laboratory have a PCL prefix. Complete copies of the SOPs may be obtained from the authors.

TABLE A.1. Standard Operating Procedures for the MAP3S/PCN

<u>Number</u>	<u>Standard Operating Procedure Title</u>
<u>Sample Identification and Custody</u>	
PCL-SOP-1	Sample Receipt and Login
PCL-SOP-2	Field Data Receipt, Filing and Login
<u>Chemical Analysis</u>	
PCL-SOP-3	pH and Conductivity
PCL-SOP-4	Anion Analysis (Ion Chromatography)
PCL-SOP-5	Automated Wet Chemistry (S-IV, NH ₄)
PCL-SOP-6	Atomic Absorption Spectrometry (not used)
PCL-SOP-7	Cation Analysis (Inductively Coupled Plasma Spectrometry)
PCL-SOP-8	Alkalinity, Total Acidity, and Gran Titration (not used)
<u>Data Base Formation and Quality Control</u>	
PCL-SOP-9	Analytical Results Login, QC Checks and Clearance
PCL-SOP-10	Precipitation Chemistry Laboratory Data Procedures
PCL-SOP-11	Computer Data Checks
PCL-SOP-12	External QA Data Clearance, Refiling and Archival
PCL-SOP-13	Computer Data Reporting
<u>MAP3S Network Management</u>	
PCN-SOP-1	Site Operator's Manual
PCN-SOP-2	MAP3S/PCN Site Audits
PCN-SOP-3	Equipment Supply for MAP3S/PCN
PCN-SOP-4	Shipping Procedure for MAP3S/PCN
PCN-SOP-5	Procedures for Recording Information in the MAP3S/PCN "Out Book"
PCN-SOP-6	Precleaning of sample collection and shipping containers
PCN-SOP-7	Preparation and distribution of pH check solution
PCN-SOP-8	Preparation of the MAP3S/PCN pH Test/Samples
PCN-SOP-9	Preparation of the MAP3S/PCN Field Blank Samples

APPENDIX B

SITE AUDITS FOR 1986 AND 1987

APPENDIX B

SITE AUDITS FOR 1986 AND 1987

An important activity in the management of MAP3S Precipitation Chemistry Network (MAP3S/PCN) is the auditing of operations at the field sites and laboratories. This audit, usually conducted by PNL personnel involved in the day-to-day management and operation of the network, serves as a QA check on the field personnel and provides site personnel onsite training opportunities. In a site audit all aspects of site operation are evaluated by the auditor. The site operator(s) are asked to perform a mock sample bucket change and pH analysis with a test solution so that the auditor can see how each procedure is done by the operator. During the audit, questions are usually asked of the operator to verify that the operator is aware of the details of the protocol and has the necessary training to respond to unusual situations. The site operator, in turn, is also given the freedom to ask the auditor for clarification of steps in the procedure with which he or she is uncertain. All items of relevance to the audit are recorded on the site audit form, which is kept on file at PNL, sent to the site operator, and published in summary report.

Audits should be carried out annually at every site. However, site audits are of lower priority than site supply and chemical analysis of the samples received from the sites. Therefore, in years with tight budgets, audits are postponed.

In the two-year period, 1986 and 1987, audits were conducted at all of the sites at least once (see Table B.1). These audits, as in the past, have turned up very few and usually only minor discrepancies from the accepted site operation protocol given in the MAP3S/PCN Site Operator's Manual. Site audit forms for the audits conducted in 1986 and 1987 are included after Table B.1.

**TABLE B.1. Site Audits of MAP3S/PCN Sites Conducted
in 1986 and 1987**

Site	Name	1986		1987	
		Date	By	Date	By
10	Whiteface			9/23/87	WRB
20	Ithaca			9/22/87	WRB
30	Penn State	10/21/86	MTD	9/21/87	WRB
40	Virginia	9/15/86	WRB	9/17/87	WRB
50	Illinois	4/16/86	MTD		
60	Brookhaven			9/25/87	WRB
70	Lewes	6/16/86	WRB	9/28/87	WRB
80	Oxford	10/31/86	MTD		
90	Oak Ridge	10/24/86	WRB		

WRB = W. R. Barchet

MTD = M. Terry Dana

SITE # 5 IllinoisAUDITOR Terry DanaSITE OPERATOR Scott Dossett, Jackie SauerDATE 4/16/86SITE MANAGER Van BowersoxPRESENT Scott Dossett, Jackie Sauer

1. Observation of Procedures/Practices

	GOOD	FAIR	POOR	REMARKS
A. Supplies Security & Control	X			
B. Sample Changing	X			
1) Preparation	X			
2) Bucket Handling En Route	X			
3) Change of Buckets	X			
4) Cleaning of Collector Pad		X		(A)
5) Handling on Return	X			
C. Lab Handling & Measurement	X			
1) Weighing Bucket	X			
2) TCM Aliquot	X			
3) TCM Fixing	X			
4) pH Aliquot	X			
5) pH Procedure	X			pH of Test Sol. <u>(None taken)</u> T of Test Sol. _____ Buffers Lo _____ Hi _____
6) Shipping Aliquot(s)	X			
7) Blank Procedure	X			
D. Storage of Samples	X			
E. Shipping Procedure	X			
1) Taping Bottles	X			
2) Blue Ice Control	X			
3) Packing	X			
4) Separation of TCM	X			

SITE # 5 IllinoisAUDITOR Terry DanaSITE OPERATOR Scott DossettDATE 4/16/86

	GOOD	FAIR	POOR	REMARKS
F. Cleaning of Reused Buckets	X			Use NADP buckets
G. Rainfall Determination	X			
Calculation of Pred. Vol.	X			
2. Discussion				
A. Operator's Manual on Hand	X			
1) Understands QA Requirements	X			
B. Understanding of Forms	X			
1) Data Log	X			
2) Rainfall	X			
3) Embarkation	X			
4) Significant Figures	X			
5) Records Unusual Items?	X			
6) Copy or Original:	X			
C. Sampling Days of Week			X	No weekends
D. Awareness of Data Reports	X			
1) Any on Hand?		X		
2) Checks Data?			X	
E. Complaints	X			
1) Deficiencies in Instructions	X			
2) Supply Problems?	X			
3) Communications Problems?	X			

SITE # 5 IllinoisAUDITOR Terry DanaSITE OPERATOR Scott DossettDATE 4/16/86

3. Additional Notes/Items of Discussion

- A. Only cleans pad every two months - at time of NADP dry-side change.
- B.
- C.
- D.
- E.
- F.
- G.

4. Major Problems

- 1. Sampling on weekends should be done.
- 2. More frequent pad cleaning should be done (or at least checked at every bucket change).

5. Summary

ISWS laboratory standards and practices are superior, quality is high, and compatible NADP procedures are always used. The MAP3S function is well organized and separate from NADP. Replacement for J. Sauer should be advised to continue these practices.

ACTION REQUIRED

- 1. We will work on getting additional funds to allow daily sampling.
- 2. Recommend more frequent pad cleaning, but NADP standard is ok.

ACTION PERFORMED

MAP3S/PCN SITE AUDIT FORM

PAGE 1 OF 3

SITE #: 3, Penn State

AUDITOR: T. Dana

SITE OPERATOR: S. Falzarano

DATE: 10/21/86

SITE MANAGER: R. DePena, D. Lamb

PRESENT: D. Lamb, Falzarano

1. Observation of Procedures/Practices

	GOOD	FAIR	POOR	REMARKS
A. Supplies Security & Control	X			
B. Sample Changing	X			
1) Preparation	X			
2) Bucket Handling En Route	X			
3) Change of Buckets	X			
4) Cleaning of Collector Pad		X		(A)
5) Handling on Return	X			
C. Lab Handling & Measurement	X			
1) Weighing Bucket	X			
2) TCM Aliquot	X			
3) TCM Fixing	X			
4) pH Aliquot	X			
5) pH Procedure [NADP]				pH of Test Sol. 4.33 #3714 T of Test Sol. 25 Buffers Lo: 4 Hi: 7
6) Shipping Aliquot(s)	X			
7) Blank Procedure	X			
D. Storage of Samples	X			
E. Shipping Procedure	X			
1) Taping Bottles	X			
2) Blue Ice Control	X			
3) Packing	X			
4) Separation of TCM	X			

SITE #: 3

AUDITOR: T. Dana

SITE OPERATOR: Falzarano

DATE: 10/21/86

	GOOD	FAIR	POOR	REMARKS
F. Cleaning of Reused Buckets	X			
G. Rainfall Determination	X			
Calculation of Pred. Vol.	X			
2. Discussion	X			
A. Operator's Manual on Hand	X			
1) Understands QA Requirements	X			
B. Understanding of Forms	X			
1) Data Log	X			
2) Rainfall	X			
3) Embarkation	X			
4) Significant Figures	X			
5) Records Unusual Items?	X			
6) Copy or Original:	X			
C. Sampling Days of Week	X			
D. Awareness of Data Reports	X			
1) Any on Hand?	X			
2) Checks Data?	X			
E. Complaints	X			
1) Deficiencies in Instructions	X			
2) Supply Problems?		X		Too many buckets on hand
3) Communications Problems?	X			

MAP3S/PCN SITE AUDIT FORM

PAGE 3 OF 3

SITE #: 3

AUDITOR: T. Dana

SITE OPERATOR: Falzarano

DATE: 10/21/86

3. Additional Notes/Items of Discussion

A. Does weekly--needs to do eventwise.

B. Needs to use new shipping labels.

4. Major Problems

None

5. Summary

NADP and CAPMoN procedures used at site--good guide for MAP3S QA

ACTION REQUIRED

See A and B above

ACTION PERFORMED

Advised of A and B above

FORM DATE 4/9/86

MAP3S/PCN SITE AUDIT FORM

PAGE 1 OF 3

SITE #: 8, Oxford, OH

AUDITOR: T. Dana

SITE OPERATOR: Pat Coyle

DATE: 10/31/86

SITE MANAGER: J. Klink

PRESENT: Klink, Coyle

1. Observation of Procedures/Practices

	GOOD	FAIR	POOR	REMARKS
A. Supplies Security & Control	X			
B. Sample Changing	X			
1) Preparation	X			
2) Bucket Handling En Route	X			
3) Change of Buckets	X			
4) Cleaning of Collector Pad	X			
5) Handling on Return	X			
C. Lab Handling & Measurement	X			
1) Weighing Bucket	X			
2) TCM Aliquot	X			
3) TCM Fixing		X		(B)
4) pH Aliquot	X			
5) pH Procedure [NADP]				pH of Test Sol. 4.31 #8828 T of Test Sol. 18C Buffers Lo: 4 Hi: 7
6) Shipping Aliquot(s)	X			
7) Blank Procedure	X			
D. Storage of Samples		X		(A)
E. Shipping Procedure	X			
1) Taping Bottles	X			
2) Blue Ice Control	X			
3) Packing	X			
4) Separation of TCM	X			

MAP3S/PCN SITE AUDIT FORM

PAGE 2 OF 3

SITE #: 8

AUDITOR: T. Dana

SITE OPERATOR: Pat Coyle

DATE: 10/31/86

	GOOD	FAIR	POOR	REMARKS
F. Cleaning of Reused Buckets	X			
G. Rainfall Determination		X		Daily chart desirable
Calculation of Pred. Vol.		X		Must match with rain record (C)
2. Discussion	X			
A. Operator's Manual on Hand	X			
1) Understands QA Requirements	X			
B. Understanding of Forms	X			
1) Data Log	X			
2) Rainfall	X			
3) Embarkation	X			
4) Significant Figures	X			
5) Records Unusual Items?	X			
6) Copy or Original:	X			
C. Sampling Days of Week	X			
D. Awareness of Data Reports	X			
1) Any on Hand?	X			
2) Checks Data?	X			
E. Complaints				
1) Deficiencies in Instructions	X			
2) Supply Problems?		X		Too many supplies at times
3) Communications Problems?	X			

MAP3S/PCN SITE AUDIT FORM

PAGE 3 OF 3

SITE #: 8

AUDITOR: T. Dana

SITE OPERATOR: Pat Coyle

DATE: 10/31/86

3. Additional Notes/Items of Discussion

- A. Had been leaving samples out of refrigerator for a day or two at times.
- B. Hadn't always done TCM fixing same day as collection.
- C. Occasionally uses other gauge for pred. volume.

4. Major Problems

None

5. Summary

Good procedures and operator transition
NADP site--site QA follows NADP

ACTION REQUIRED

Keep samples in refrigerator all times--fix TCM promptly
Make rain data sheet agree with pred. volume calculation

ACTION PERFORMED

Advised operator

FORM DATE 4/9/86

MAP3S/PCN SITE AUDIT FORM

PAGE 1 OF 3

SITE #: 04

AUDITOR: WR Barchet

SITE OPERATOR: Cindy Donoghue

DATE: 9/17/87

SITE MANAGER: Jim Galloway, Bill Keene

PRESENT: Bill Keene, Cindy Donoghue

1. Observation of Procedures/Practices

	GOOD	FAIR	POOR	REMARKS
A. Supplies Security & Control	X			See note A
B. Sample Changing				
1) Preparation	X			All supplies at site
2) Bucket Handling En Route	X			At site; in bags
3) Change of Buckets	X			Downwind
4) Cleaning of Collector Pad	X			Wiped and inspected
5) Handling on Return	X			Tape lid; in truck cab
C. Lab Handling & Measurement				See note B
1) Weighing Bucket	X			Ohaus 25 kg triple beam
2) TCM Aliquot	X			20 ml pipette with bulb
3) TCM Fixing	X			In hood, autopipetters, 1 ml
4) pH Aliquot	X			Reuses plastic vials
5) pH Procedure	X See note C			pH of Test Sol. <u>4.57</u> T of Test Sol.: <u>25.5</u> Buffers Lo: <u>4.00</u> Hi: <u>7.00</u>
6) Shipping Aliquot(s)	X			
7) Blank Procedure				Hasn't had opportunity to do one yet.
D. Storage of Samples	X			Dedicated refrigerator
E. Shipping Procedure				
1) Taping Bottles	X			
2) Blue Ice Control	X			Bagged
3) Packing	X			Supplies in separate, locked storage area
4) Separation of TCM	X			Bagged separately

SITE #: 04

AUDITOR: WR Barchet

SITE OPERATOR: Cindy Donoghue

DATE: 9/17/87

	GOOD	FAIR	POOR	REMARKS
F. Cleaning of Reused Buckets				Not reused but saved
G. Rainfall Determination	X			Wedge & weighing gauges
Calculation of Pred. Vol.				See note E
2. Discussion				
A. Operator's Manual on Hand				Yes, needs own manual
1) Understands QA Requirements	X			
B. Understanding of Forms				See note D
1) Data Log	X			Begun in field
2) Rainfall	X			Needs experience to become familiar
3) Embarkation	X			Added to w/each sample
4) Significant Figures	X			
5) Records Unusual Items?	X			Conscientious; probably will make notes
6) Copy or Original:				
C. Sampling Days of Week	X			All days
D. Awareness of Data Reports				
1) Any on Hand?				Yes
2) Checks Data?				Limited; not part of operator duties
E. Complaints				
1) Deficiencies in Instructions				None yet noted
2) Supply Problems?	None			Blue Ice needed
3) Communications Problems?				None; will give us office number

SITE #: 04

AUDITOR: WR Barchet

SITE OPERATOR: Cindy Donoghue

DATE: 9/17/87

3. Additional Notes/Items of Discussion

- A. Field shed in need of repair; door does not lock. New shed will be part of site upgrade at which time AC power will be brought to site and access road improved.
- B. After removing lid, bucket kept covered with plastic wrap. pH and conductivity aliquots covered with plastic wrap while waiting for temperature equilibration.
- C. Remeasured old sample #012840; original field pH = 4.37. Buffer solutions by Fischer Chem Alert. Conductivity of DIW rinse water checked at start of procedure. Orion Res. 701A digital pH meter.
- D. Suggest data logs, embarkation and rainfall forms be kept in 3-ring binder while being used in the laboratory.
- E. Predicted vol < measured vol almost always. May indicate problem in bucket size or calibration of rain gauge.

4. Major Problems

Trees (locust) to west of site will soon intersect 45° cone. Plan being approved by University of VA to bring AC power to site, improve road and cut these and other nearby trees.

5. Summary

Operator on job about 2 months. Very conscientious. Needs experience with some operations (field blanks, QA samples, shipping). Questions can be handled by Keene or M. Castro (former operator).

ACTION REQUIRED

Cut back/down trees to west and others near site. Suggest calibration of weighing raingauge be checked and reported. PNL to send new operator's manual.

ACTION PERFORMED

MAP3S/PCN SITE AUDIT FORM

PAGE 1 OF 3

SITE #: 03

AUDITOR: WR Barchet

SITE OPERATOR: Steve Falzarano

DATE: 9/21/87

SITE MANAGER: Dennis Lamb

PRESENT: Steve Falzarano,
Raja Elsalem

1. Observation of Procedures/Practices

	GOOD	FAIR	POOR	REMARKS
A. Supplies Security & Control	X			Own lab room. Locked field shed.
B. Sample Changing				See note A.
1) Preparation	X			Buckets & lids in lab
2) Bucket Handling En Route	X			Left in bag
3) Change of Buckets	X			Checked wind direction
4) Cleaning of Collector Pad	X			Alcohol and wipe
5) Handling on Return	X			Bagged bucket in lab
C. Lab Handling & Measurement				See note B.
1) Weighing Bucket	X			TORBAL Model DH-2.
2) TCM Aliquot	X			5 ml autopipette used to draw sample.
3) TCM Fixing	X			Sample bottle preloaded with 2 ml TCM.
4) pH Aliquot	X			Drawn with syringe. See note C.
5) pH Procedure	See note D			Test Sol. pH <u>4.28</u> (<u>4.3±0.1</u>) T of Test Sol.: <u>25°C</u> Buffers Lo: <u>4.0</u> Hi: <u>7.0</u>
6) Shipping Aliquot(s)	X			
7) Blank Procedure	X			See note E.
D. Storage of Samples	X			Dedicated refrig. in lab.
E. Shipping Procedure				
1) Taping Bottles	X			Taped before storage.
2) Blue Ice Control	X			May or may not be bagged.
3) Packing	X			
4) Separation of TCM	X			Bagged separately

SITE #: 03

AUDITOR: WR Barchet

SITE OPERATOR: Steve Falzarano

DATE: 9/21/87

	GOOD	FAIR	POOR	REMARKS
F. Cleaning of Reused Buckets	NA			Not used
G. Rainfall Determination	X			See note F
Calculation of Pred. Vol.				
2. Discussion				
A. Operator's Manual on Hand				
1) Understands QA Requirements				In lab, but needs another
B. Understanding of Forms				
1) Data Log	X			Begun w/notes on raingauge
2) Rainfall	X			Strip chart
3) Embarkation	X			
4) Significant Figures	X			
5) Records Unusual Items?	X			Yes; debris/insects common
6) Copy or Original:				
C. Sampling Days of Week	X			All days
D. Awareness of Data Reports				
1) Any on Hand?	X			All on hand
2) Checks Data?	X			83-86 in LOTUS
E. Complaints				
1) Deficiencies in Instructions				None
2) Supply Problems?				Hold off on lids.
3) Communications Problems?				None

SITE #: 03

AUDITOR: WR Barchet

SITE OPERATOR: Steve Falzarano

DATE: 9/21/87

3. Additional Notes/Items of Discussion

- A. Valid sample in bucket #092130; field pH = 3.822, conductivity = 70.3 μ mhos
- B. Raja Elsalem does the lab work. Steve Falzarano does the field work. Raja Elsalem available to do field work if Steve is unavailable. Dick Thompson is another backup person for both field and lab work.
- C. Drawing pH aliquot with syringe which requires that operator's hands and arms be put inside bucket, seems to increase the potential for contamination from skin/clothing debris.
- D. Orion 701A digital pH with Beckman probe. Beckman RC16B2 conductivity bridge.
- E. Steve was not aware of the 9/86 change in procedure for field blanks.
- F. Uses 640 factor but has noted this consistently leads to low predicted volumes. Suggests we go to simple funnel gauge for ppt amount; claims more accurate than Belfort weighing gauge.

4. Major Problems

None

5. Summary

Steve is an experienced site operator. Site is in good, secure location (Scotia Range) along with NADP and CAPMoN samplers. Steve would prefer a standard sample collection time but felt CAPMoN's 7-9 am was too restrictive.

ACTION REQUIRED

- 1) Send Lamb copy of field blank procedure and site operator manual.

ACTION PERFORMED

FORM DATE 4/9/86

MAP3S/PCN SITE AUDIT FORM

PAGE 1 OF 3

SITE #: 02 - Ithaca

AUDITOR: WR Barchet

SITE OPERATOR: Tom Butler

DATE: 9/22/87

SITE MANAGER: Gene Likens

PRESENT: Tom Butler

1. Observation of Procedures/Practices

	GOOD	FAIR	POOR	REMARKS
A. Supplies Security & Control	X			See note A
B. Sample Changing				
1) Preparation	X			
2) Bucket Handling En Route	X			Dbt-bagged. Clean, dry bucket.
3) Change of Buckets	X			Dry bucket also changed. See note B.
4) Cleaning of Collector Pad	X			Deionized water used to wash sampler.
5) Handling on Return	X			Bagged; held in child's seat.
C. Lab Handling & Measurement				
1) Weighing Bucket	X			Sartorius Univ. U5000D Does own tare of bucket.
2) TCM Aliquot	X			All samples poured immediately into bottles.
3) TCM Fixing	X			2 ml plastic-bulb pipette. Will store in ventilated hood.
4) pH Aliquot	X			Only a few ml needed. Radiometer PHM82
5) pH Procedure	X See Note C			pH of Test Sol. <u>4.64</u> T of Test Sol.: <u>22°C</u> Buffers Lo: <u>4.00</u> Hi: <u>7.00</u>
6) Shipping Aliquot(s)	X			
7) Blank Procedure	X			Not aware of change in procedure.
D. Storage of Samples	X			Share refrig. in lab.
E. Shipping Procedure				
1) Taping Bottles	X			
2) Blue Ice Control	X			2 in summer, 1 in spring and fall.
3) Packing	X			
4) Separation of TCM	X			Bagged separately

MAP3S/PCN SITE AUDIT FORM

PAGE 2 OF 3

SITE #: 02 - Ithaca

AUDITOR: WR Barchet

SITE OPERATOR: Tom Butler

DATE: 9/22/87

	GOOD	FAIR	POOR	REMARKS
F. Cleaning of Reused Buckets	X			Uses cleaned buckets for dry side.
G. Rainfall Determination	X			Standard NWS gauge, note D
Calculation of Pred. Vol.				Feels 640 too small.
2. Discussion				
A. Operator's Manual on Hand				Kept in desk not at site or lab
1) Understands QA Requirements	X			
B. Understanding of Forms				
1) Data Log	X			
2) Rainfall	X			Indicates sample collection time on form.
3) Embarkation	X			
4) Significant Figures	X			
5) Records Unusual Items?	X			
6) Copy or Original:				
C. Sampling Days of Week	X			Every day - see note E
D. Awareness of Data Reports				
1) Any on Hand?	Yes			
2) Checks Data?	Yes			Trying to get all MAP3S data from ADS.
E. Complaints				
1) Deficiencies in Instructions				None
2) Supply Problems?				None
3) Communications Problems?				None

SITE #: 02 - Ithaca

AUDITOR: WR Barchet

SITE OPERATOR: Tom Butler

DATE: 9/22/87

3. Additional Notes/Items of Discussion

- A. Field supplies in padlocked cabinets and in NDDN trailer. Lab at Cornell kept locked when unattended. Site is 12 miles SW of Cornell University on Connecticut Hill near Endfield, NY.
- B. Elevated platform for collector limits access to only the west side of sample bucket and creates potential for sample contamination if the wind is strong from west during a bucket change. Butler was confident this posed no problem.
- C. Remeasured sample 072880; previous PNL lab pH = 4.67.
- D. Tipping bucket record used to obtain time distribution of precipitation but NWS gauge is used for total event volume. A Belfort weighing gauge is available but has not been deployed.
- E. Butler is only site operator, no backup is available. However he has trained a friend to do the bucket change and transfer sample to bottle(s). His friend stores samples in his refrigerator until Butler returns and does the pH measurement. Butler uses personal automobile for all site visits (he gets about \$7/trip for mileage). Butler pays friend \$10 per sample when he is unavailable.
- F. Trees were removed west (upslope) and north of site in June to enlarge the clearing to accommodate the NDDN site. This is the first major change at the site since it started in 1976.

4. Major Problems

None

5. Summary

The Ithaca site is one of the best ran, most consistently operated site in the network. Present arrangement with Butler as site operator and Likens as an absentee site manager works because Butler makes it happen.

ACTION REQUIRED

ACTION PERFORMED

TCM solution stored in fume hood.

MAP3S/PCN SITE AUDIT FORM

PAGE 1 OF 3

SITE #: 01 - Whiteface Mt.

AUDITOR: WR Barchet

SITE OPERATOR: Marc DuBois

DATE: 9/23/87

SITE MANAGER: John Kadlecek

PRESENT: Marc DuBois

1. Observation of Procedures/Practices

	GOOD	FAIR	POOR	REMARKS
A. Supplies Security & Control	X			Now have own lab building
B. Sample Changing				See note A
1) Preparation	X			
2) Bucket Handling En Route	X			Hand carried to site
3) Change of Buckets	X			
4) Cleaning of Collector Pad	X			See note B
5) Handling on Return	X			Hand carried to lab
C. Lab Handling & Measurement				
1) Weighing Bucket	X			OHAUS Model 11190
2) TCM Aliquot	X			Pipette with rubber bulb from beaker
3) TCM Fixing	X			Pipette with rubber bulb in hood
4) pH Aliquot	X			Pours into vials
5) pH Procedure	See Note C			pH of Test Sol. <u>4.68</u> T of Test Sol.: <u>22.6°C</u> Buffers Lo: <u>4.00</u> Hi: <u>7.00</u>
6) Shipping Aliquot(s)	X			Pours direct into bottles
7) Blank Procedure	X			Few periods of 168 consecutive dry hours
D. Storage of Samples	X			Shared refrigerator
E. Shipping Procedure				
1) Taping Bottles	X			
2) Blue Ice Control	X			
3) Packing	X			
4) Separation of TCM	X			Bagged separately

SITE #: 01 - Whiteface Mnt.

AUDITOR: WR Barchet

SITE OPERATOR: Marc DuBois

DATE: 9/22/87

	GOOD	FAIR	POOR	REMARKS
F. Cleaning of Reused Buckets	X			See note D
G. Rainfall Determination				See note E
Calculation of Pred. Vol.	NA			
2. Discussion				
A. Operator's Manual on Hand				
1) Understands QA Requirements	X			See note C
B. Understanding of Forms				
1) Data Log	X			
2) Rainfall	X			Done weekly when NTN sample collected
3) Embarkation	X			
4) Significant Figures				
5) Records Unusual Items?	X			
6) Copy or Original:				
C. Sampling Days of Week				Every day - see note F
D. Awareness of Data Reports				
1) Any on Hand?	yes			
2) Checks Data?				sometimes
E. Complaints				
1) Deficiencies in Instructions				none
2) Supply Problems?				Out of buckets
3) Communications Problems?				Does not call; waits for monthly embarkation form

SITE #: 01 - Whiteface Mt.

AUDITOR: WR Barchet

SITE OPERATOR: Marc DuBois

DATE: 9/23/87

3. Additional Notes/Items of Discussion

- A. No bucket change was performed because "event" was still in progress. Walked and talked way through bucket change.
- B. Pad on new ACM sample did not seal completely where there was a wrinkle in the plastic covering over the foam.
- C. ORION Model 611 pH meter. Would prefer to have a quality control standard to check pH reading and condition of probe.
- D. Had to clean used buckets because they were out of clean buckets: scrub with deionized water (DIW); rinse frequently; soak in DIW until needed.
- E. Uses NTN weekly strip chart for determining time and amount of precipitation. Does not have a separate rain gauge for MAP3S.
- F. Only Marc DuBois is trained as a site operator. Tim Brown does sample collection (changes bucket, stores bucket in refrigerator) when DuBois unavailable.

4. Major Problems

None

5. Summary

The colocation of this site with NTN, MCCP and NOAA dry deposition offers great benefits through the various QA/QC checks on field procedures. DuBois has a solid grasp of all sampling protocols. This site will continue to be well operated as long as DuBois is the operator.

ACTION REQUIRED

Replace the lid pad on collector.

ACTION PERFORMED

MAP3S/PCN SITE AUDIT FORM

PAGE 1 OF 3

SITE #: 07 - Lewes

AUDITOR: WR Barchet

SITE OPERATOR: Patti Salevan

DATE: 9/28/87

SITE MANAGER: Joe Scudlark

PRESENT: P. Salevan, J. Scudlark,
H. Moses (DOE/OHER)

1. Observation of Procedures/Practices

	GOOD	FAIR	POOR	REMARKS
A. Supplies Security & Control	X			Dedicated lab space
B. Sample Changing				See note A
1) Preparation	X			
2) Bucket Handling En Route	X			Double bagged
3) Change of Buckets	X			
4) Cleaning of Collector Pad	X			
5) Handling on Return	X			Double bagged
C. Lab Handling & Measurement				See note B
1) Weighing Bucket	X			OHAUS 2610 Triple beam
2) TCM Aliquot	X			Uses plastic syringe
3) TCM Fixing	X			1-ml autopipette
4) pH Aliquot	X			Uses plastic syringe
5) pH Procedure	See note C			pH of Test Sol. <u>4.28</u> (PNL <u>4.67</u>) T of Test Sol.: <u>22°C</u> Buffers Lo: <u>4.00</u> Hi: <u>4.63</u>
6) Shipping Aliquot(s)	X			Pours direct; archives excess at room temp.
7) Blank Procedure	X			Rinses side, sloshes in bucket
D. Storage of Samples	X			Shares refrigerator
E. Shipping Procedure				
1) Taping Bottles	X			
2) Blue Ice Control	X			Bagged
3) Packing	X			
4) Separation of TCM	X			Bagged separately

MAP3S/PCN SITE AUDIT FORM

PAGE 2 OF 3

SITE #: 07 - Lewes

AUDITOR: WR Barchet

SITE OPERATOR: Patti Salevan

DATE: 9/28/87

	GOOD	FAIR	POOR	REMARKS
F. Cleaning of Reused Buckets	X			DIW rinse and soak; only if needed
G. Rainfall Determination	X			See note D
Calculation of Pred. Vol.				
2. Discussion				
A. Operator's Manual on Hand				
1) Understands QA Requirements	X			Kept with log forms
B. Understanding of Forms				See note E
1) Data Log	X			
2) Rainfall	X			Done monthly
3) Embarkation	X			
4) Significant Figures				OK
5) Records Unusual Items?	X			Bird dropping, high wind
6) Copy or Original:	X			Original
C. Sampling Days of Week	X			Every day
D. Awareness of Data Reports				
1) Any on Hand?	X			
2) Checks Data?	X			Computer data base
E. Complaints				None
1) Deficiencies in Instructions				
2) Supply Problems?				
3) Communications Problems?				

SITE #: 07 - Lewes

AUDITOR: WR Barchet

SITE OPERATOR: Patti Salevan

DATE: 9/28/87

3. Additional Notes/Items of Discussion

- A. Scudlark has been collecting samples because Salevan has been prohibited by her physician from lifting heavy objects.
- B. All rain chemistry samples handled in dedicated room. This is to keep these samples separate from trace metal samples which require acid washing and fixing.
- C. Orion Model 701A digital pH meter. Uses meter on mv scale. First measures emf of sample (triplicate), then chooses 2 buffers that bracket sample emf and measures emf's of the 2 buffers. Calculates sample pH from linear interpolation scaled to buffer and sample emf's. Measured sample 072880 424-04 which had PNL pH = 4.67. No explanation for such a large discrepancy. Scudlark will do additional testing of pH meter.
- D. Uses 8-day chart on Belfort weighing gauge; checks event ppt amount with funnel gauge. Ppt amount logged monthly; charts discarded.
- E. Use their own log form (attached) for original data entry; transcribe to MAP3S log form at end of month. Includes an indication of trajectory and weather during an event.

4. Major Problems

None

5. Summary

Site operation follows protocol and common sense for maintaining sample integrity.

ACTION REQUIRED

Test pH meter with low ionic strength solutions (Scudlark). Remeasure pH of sample 072880 424-4 again (PNL).

ACTION PERFORMED

Scudlark (10/7/87) found that the pH meter calibration was off and the probe was probably defective. When meter was recalibrated with new probe, pH = 4.61 compared to 4.67 as measured at PNL 10/2/87.

MAP3S/PCN SITE AUDIT FORM

PAGE 1 OF 3

SITE #: 9, Oak Ridge

AUDITOR: Terry Dana

SITE OPERATOR: J. Owens

DATE: 3/16/88

SITE MANAGER: S. Lindberg

PRESENT: J. Owens

1. Observation of Procedures/Practices

	GOOD	FAIR	POOR	REMARKS
A. Supplies Security & Control	X			Has own lab
B. Sample Changing	X			No weekends (A)
1) Preparation	X			
2) Bucket Handling En Route	X			
3) Change of Buckets	X			
4) Cleaning of Collector Pad	X			Each event
5) Handling on Return	X			Uses bag and rubber bands
C. Lab Handling & Measurement	X			
1) Weighing Bucket	X			
2) TCM Aliquot	X			Keeps TCM in hood
3) TCM Fixing	X			Post sample division
4) pH Aliquot	X			
5) pH Procedure	X			pH Test Sol. <u>4.40</u> T of Test Sol.: <u>---</u> Buffers Lo: <u>4</u> Hi: <u>7</u>
6) Shipping Aliquot(s)	X			
7) Blank Procedure	X			
D. Storage of Samples	X			Own refrigerator
E. Shipping Procedure	X			
1) Taping Bottles	X			
2) Blue Ice Control	X			
3) Packing	X			
4) Separation of TCM	X			In hood

SITE #: 9

AUDITOR: Terry Dana

SITE OPERATOR: Owens

DATE: 3/16/88

	GOOD	FAIR	POOR	REMARKS
F. Cleaning of Reused Buckets	X			Not done yet
G. Rainfall Determination	X			Weekly charts (8)
Calculation of Pred. Vol.	X			Will do and enter on form
2. Discussion				
A. Operator's Manual on Hand	X			
1) Understands QA Requirements	X			
B. Understanding of Forms				
1) Data Log	X			
2) Rainfall	X			
3) Embarkation	X			
4) Significant Figures	X			
5) Records Unusual Items?	X			
6) Copy or Original:	X			
C. Sampling Days of Week		X		Weekdays only (A)
D. Awareness of Data Reports	X			
1) Any on Hand?	X			
2) Checks Data?	X			
E. Complaints				
1) Deficiencies in Instructions	X			
2) Supply Problems?	X			
3) Communications Problems?	X			

MAP3S/PCN SITE AUDIT FORM

PAGE 3 OF 3

SITE #: 9

AUDITOR: Terry Dana

SITE OPERATOR: J. Owens

DATE: 3/16/88

3. Additional Notes/Items of Discussion

- A. Does not sample on weekends but procedure is being worked out, effective in several months.
- B. PNL may consider providing additional Belfort with daily chart.

4. Major Problems

None

5. Summary

Excellent site operation, especially record keeping and laboratory procedures.

ACTION REQUIRED

None.

ACTION PERFORMED

FORM DATE 4/9/86

MAP3S/PCN SITE AUDIT FORM

PAGE 1 OF 3

SITE #: 06 - Brookhaven Nat. Lab.

AUDITOR: WR Barchet

SITE OPERATOR: John McNeil

DATE: 9/25/87

SITE MANAGER: Bob Brown

PRESENT: Bob Brown, Roger Tanner,
Bob Wilson

1. Observation of Procedures/Practices

	GOOD	FAIR	POOR	REMARKS
A. Supplies Security & Control	X			See note A
B. Sample Changing				See note B
1) Preparation	X			
2) Bucket Handling En Route	X			As received, in van
3) Change of Buckets		X		Van parks very close to sampler
4) Cleaning of Collector Pad	X			
5) Handling on Return	X			Lid bag covers bucket
C. Lab Handling & Measurement				See note C
1) Weighing Bucket	X			Mettler PL3000; reweighs empty bucket
2) TCM Aliquot	X			Uses syringe
3) TCM Fixing	X			2-ml TCM pre-added to bottle
4) pH Aliquot	X			Uses syringe
5) pH Procedure	See note D			pH of Test Sol. <u>4.70, 4.69</u> T of Test Sol.: <u>23°C</u> Buffers Lo: <u>4.0</u> Hi: <u>7.01</u>
6) Shipping Aliquot(s)	X			Pours direct
7) Blank Procedure	X			Bucket provided by McNeil, water added at Hot Lab.
D. Storage of Samples	X			Share refrigerator
E. Shipping Procedure				See note E
1) Taping Bottles				
2) Blue Ice Control				
3) Packing				
4) Separation of TCM				

SITE #: 06 - Brookhaven

AUDITOR: WR Barchet

SITE OPERATOR: John McNeil

DATE: 9/25/87

	GOOD	FAIR	POOR	REMARKS
F. Cleaning of Reused Buckets				
G. Rainfall Determination	X			Tipping bucket
Calculation of Pred. Vol.	X			
2. Discussion				See note F
A. Operator's Manual on Hand				
1) Understands QA Requirements				
B. Understanding of Forms				
1) Data Log				Atmos. Sci. begins; Chem. Group completes
2) Rainfall				
3) Embarkation				Sent by Chemistry Group
4) Significant Figures				
5) Records Unusual Items?				
6) Copy or Original:				
C. Sampling Days of Week	X			Weekend samples stored in fridge & analyzed on Mon.
D. Awareness of Data Reports				Not determined
1) Any on Hand?				
2) Checks Data?				
E. Complaints				None
1) Deficiencies in Instructions				
2) Supply Problems?				
3) Communications Problems?				

SITE #: 06 - Brookhaven

AUDITOR: WR Barchet

SITE OPERATOR: John McNeil

DATE: 9/25/87

3. Additional Notes/Items of Discussion

- A. Buckets and lids and data log forms kept at bldg. 51 (Atmos. Sci.). Embarkation forms, sample bottles and shipping supplies kept at bldg. 801 (Hot Lab).
- B. Bob Brown doing sample collection while John McNeil out of town on business. He (or John) changes sample bucket and provides meteorological data on log forms.
- C. Sample bucket taken to Hot Lab for pH measurement, pouring into bottles, storage and shipping. Paul Klotz or Chuck Bachsmith usually do these activities. Both were unavailable for this audit. Bob Wilson did pH measurement on test sample. Buckets stored in refrigerator until Paul or Chuck can do pH measurement.
- D. Beckman Model 4500 with Orion Ross pH probe. Sample 424-04 072880 (pH = 4.67) remeasured. Usually use constant temperature bath at 20°C; bath not working today so pH measurement at room temperature.
- E. Neither Bob Wilson or Roger Tanner were familiar with shipping procedures so this portion of audit was postponed until Paul Klotz could be interviewed by phone on 9/30/87.
- F. Most information in this section obtained during telephone call to Paul Klotz on 9/30/87.

4. Major Problems

None

5. Summary

Division of activities between Atmospheric Sciences (sample solution) and Analytical Chemistry (pH, shipping) is unusual among MAP3S sites but appears to be a satisfying arrangement.

ACTION REQUIRED

ACTION PERFORMED

MAP3S/PCN SITE AUDIT FORM

PAGE 1 OF 3

SITE #: 5, Illinois

AUDITOR: W. R. Barchet

SITE OPERATOR: Mike Snider

DATE: 10/28/88

SITE MANAGER: Van Bowersox

PRESENT: Mike Snider, Jackie Sauer

1. Observation of Procedures/Practices

	GOOD	FAIR	POOR	REMARKS
A. Supplies Security & Control	X			See Note A.
B. Sample Changing				See Note B.
1) Preparation	X			Drum chart changed in shelter ("cave")
2) Bucket Handling En Route	X			Bagged
3) Change of Buckets	X			Downwind. Visual examination. Lid hammered on. See Note C.
4) Cleaning of Collector Pad		X		1 per month when cold. See Note D.
5) Handling on Return	X			Sample kept in cooler until analyzed and prepared for shipping.
C. Lab Handling & Measurement				
1) Weighing Bucket	X			Mettler PC 4400
2) TCM Aliquot	X			
3) TCM Fixing	X			Prespiked bottles. Bottles are marked with current depth. Also a formaldehyde spike.
4) pH Aliquot	X			Poured
5) pH Procedure See Note E.	X			pH of Test Sol. _____ T of Test Sol. <u>24.7C (room)</u> Buffers Lo: ____ Hi: ____
6) Shipping Aliquot(s)				Pours
7) Blank Procedure				
D. Storage of Samples	X			Walk in cold room

MAP3S/PCN SITE AUDIT FORM

PAGE 2 OF 3

SITE #: 5

AUDITOR: W. R. Barchet

SITE OPERATOR: Mike Snider

DATE: 10/28/88

	GOOD	FAIR	POOR	REMARKS
E. Shipping Procedure	X			
1) Taping Bottles				Use parafilm for wrapping lid and neck
2) Blue Ice Control				3 used in each box
3) Packing				Sent by 6th or 1st sample
4) Separation of TCM				Zip lock bags
F. Cleaning of Reused Buckets	X			Follows NADP/NTN protocol
G. Rainfall Determination	X			
Calculation of Pred. Vol.				Does not do
2. Discussion				
A. Operator's Manual on Hand				Send another copy for use in lab
1) Understands QA Requirements				
B. Understanding of Forms				
1) Data Log	X			Done partially by Jackie
2) Rainfall	X			Done by Mike
3) Embarkation	X			Jackie Sauer
4) Significant Figures	X			
5) Records Unusual Items?				
6) Copy or Original:				
C. Sampling Days of Week	X			7 days
D. Awareness of Data Reports				
1) Any on Hand?	X			Yes
2) Checks Data?	X			Yes

MAP3S/PCN SITE AUDIT FORM

PAGE 3 OF 3

SITE #: 5

AUDITOR: W. R. Barchet

SITE OPERATOR: Mike Snider

DATE: 10/28/88

	GOOD	FAIR	POOR	REMARKS
E. Complaints				
1) Deficiencies in Instructions				
2) Supply Problems?				None
3) Communications Problems?				None

3. Additional Notes/Items of Discussion

- A. All field supplies kept in underground storage area at site. Lab supplies are in separate MAP3S drawer in ISWS lab room. Rain gauge drums with new charts kept here.
- B. MAP3S and NADP/NTN collectors operated from the same rain sensor attached for NADP/NTN collector.
- C. Collector lid is opened by mechanically tripping the clutch; this allows MAP3S samples to be collected daily without opening the NADP/NTN weekly collector.
- D. Mike was not aware that manual calls for daily wipe of lid-pad.
- E. Procedure is same as used for NADP/NTN. Several pH-check, test, and buffer measurements made along with sample.

4. Major Problems

None

5. Summary

Site is well operated. Mike Snider handles all field operations and rain gauge strip chart decoding. Jackie Saver does all lab work and sample shipment.

ACTION REQUIRED

Clean lid-pad whenever bucket is changed.

ACTION PERFORMED

Will begin lid-pad cleaning with each bucket change.

APPENDIX C

DATA EDITING PROCEDURE

APPENDIX C

DATA EDITING PROCEDURE

TABLE C.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 C.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.

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