

NADP QA Plan 2006-01

QUALITY ASSURANCE PLAN CENTRAL ANALYTICAL LABORATORY, 2006



NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

A Cooperative Research Support Program of the
State Agricultural Experiment Stations (NRSP-3)
Federal State Agencies
and Private Research Organizations



In 2005, scientists, students, educators, and others interested in the National Atmospheric Deposition Program (NADP) logged more than 310,000 sessions and viewed nearly 93,000 maps on the NADP Web site. Users downloaded 18,564 data files from this site, which now annually receives more than 1.2 million hits. These data are used to address important questions about the impact of the wet deposition of nutrients on eutrophication in coastal estuarine environments; the relationship between wet deposition, the health of unmanaged forests, and the depletion of base cations from forest soils; the impact of pollutant emissions changes on precipitation chemistry; and the rate at which precipitation delivers mercury to remote lakes and streams.

The NADP was organized in 1977 under State Agricultural Experiment Station (SAES) leadership to address the problem of atmospheric deposition and its effects on agricultural crops, forests, rangelands, surface waters, and other natural and cultural resources. In 1978, sites in the NADP precipitation chemistry network first began collecting one-week, wet-only deposition samples analyzed by the Central Analytical Laboratory (CAL) at the Illinois State Water Survey. The network was established to provide data on amounts, temporal trends, and geographic distributions of the atmospheric deposition of acids, nutrients, and base cations by precipitation. The NADP initially was organized as SAES North Central Regional Project NC-141, which all four SAES regions endorsed as Interregional Project IR-7 in 1982. A decade later, IR-7 was reclassified as National Research Support Project NRSP-3, which it remains.

In October 1981, the federally supported National Acid Precipitation Assessment Program (NAPAP) was established to increase understanding of the causes and effects of acidic precipitation. This program sought to establish a long-term precipitation chemistry network of sampling sites distant from point source influences. Because of its experience in organizing and operating a national-scale network, the NADP agreed to coordinate operation of NAPAP's National Trends Network (NTN). To benefit from identical siting criteria and operating procedures and a shared analytical laboratory, NADP and NTN merged with the designation NADP/NTN. Many NADP/NTN sites were supported by the U.S. Geological Survey, NAPAP's lead federal agency for deposition monitoring. Under Title IX of the federal Clean Air Act Amendments of 1990, NAPAP continues. Today there are more than 250 sites in the network, and the network designation has been shortened to NTN.

In October 1992, the Atmospheric Integrated Research Monitoring Network (AIRMoN), currently with seven sites, joined the NADP. AIRMoN sites collect samples daily when precipitation occurs. Samples are refrigerated until analysis at the CAL for the same constituents measured in NTN samples. The AIRMoN seeks to investigate pollutant source/receptor relationships and the effect of emissions changes on precipitation chemistry, combining measurements with atmospheric models. The AIRMoN also evaluates sample collection and preservation methods.

In January 1996, the Mercury Deposition Network (MDN), currently with more than 90 sites, joined the NADP. MDN sites collect wet-only deposition samples that are sent to the MDN analytical laboratory at Frontier Geosciences, Inc. The MDN was formed to provide data on the wet deposition of mercury to surface waters, forested watersheds, and other receptors. Forty-five states and eight Canadian provinces have advisories against consuming fish from lakes with high mercury concentrations in fish tissues. MDN data enable researchers to investigate the link between mercury in precipitation and this problem.

The NADP receives support from the U.S. Geological Survey; Environmental Protection Agency; National Park Service; National Oceanic and Atmospheric Administration; U.S. Department of Agriculture - Forest Service; U.S. Fish & Wildlife Service; Tennessee Valley Authority; Bureau of Land Management; and U.S. Department of Agriculture - Cooperative State Research, Education, and Extension Service under agreement 2002-39138-11964. Additional support is provided by other federal, state, local, and tribal agencies, State Agricultural Experiment Stations, universities, and nongovernmental organizations. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the authors and do not necessarily reflect the views of the U.S. Department of Agriculture or any other sponsor.

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Quality Assurance Plan

Version 2.0, June 1, 2006

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Quality Assurance Plan Approval Form

The Quality Assurance Plan has been reviewed and approved by the following authorized Illinois State Water Survey signatories for quality assurance documents.

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List of CAL QAPP revisions

B-2.0, Table 2	Revised sample dilution procedures implemented based on Network Operations Subcommittee (NOS) 2002 audit team recommendation.
B-4.0	Revised procedure for calculating Method Detection Limits (MDLs).
B-4.0, Table 3	Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) replaced Atomic Adsorption Spectrometer as of January 2004. (Other changes were made throughout the document to reflect this change.)
B-4.0, Table 5	Table of historic MDLs updated.
B-4.0, Table 6	Percentiles for concentration values updated.
B-5.0	Records retention period changed to 2.5 years after date of analysis.
C-1.0	Selection of samples for random reanalysis changed. Samples are selected automatically by the Laboratory Information Management System (LIMS) and not by the QA Specialist.
D	Chapter revised extensively with updated flowcharts and other information to reflect functionality of LIMS system implemented since last revision.
All sections	Minor editorial changes were made throughout the document to clarify procedures.

Acknowledgments

The authors would like to thank John Ingrum for his detailed review of the NADP CAL data section and Tom Bergerhouse for his review of the computer programs and LIMS used by the CAL. Thanks also to Pam Bedient , the CAL Administrative Coordinator, without whose help this document could never have been completed. Thanks also go to all previous reviewers and contributors who have helped make this document as complete and accurate as possible.

Table of Contents

Page

Quality Assurance Plan Document History Report	iii
Quality Assurance Plan Approval Form	v
Quality Assurance Plan Distribution List	vii
Acknowledgments	ix
Table of Contents	xi
List of Figures	xiii
List of Tables	xiii
Acronyms and Abbreviations	xiv
A. Project Management	1
1.0 Purpose of Plan	1
2.0 Management and Organization	2
3.0 Elements of NADP CAL Quality System	4
4.0 Personnel Qualifications and Training	4
5.0 Laboratory Facilities	5
B. Laboratory Operations	7
1.0 Program Objectives	7
2.0 Sample Processing	7
3.0 Site Resupply	7
4.0 Sample Chemical Analysis	10
5.0 Record Archives	19
6.0 General Laboratory Procedures	19
7.0 Instrument Procedures	20
8.0 Analytical Blanks	20
9.0 Sample Precision	21
10.0 Sample Storage	22
11.0 Data Verification	23
12.0 Preventive Maintenance/Service	23

	<i>Page</i>
C. Laboratory QA/QC Procedures.....	25
1.0 Performance and Systems Audits	25
2.0 Screening and Reporting Noncompliance with Data Quality Objectives.....	26
3.0 Corrective Actions	26
D. Data Management Operations.....	33
1.0 Computer Hardware and Software.....	33
2.0 NTN Description.....	34
3.0 AIRMoN-wet Description	40
E. Terms and Definitions.....	45
F. Bibliography	49
Appendix A. List of CAL Standard Operating Procedures (SOPs)	51
Appendix B. Control and Warning Limits For Internally Prepared QC Solutions	57

List of Figures

Page

Figure 1.	Central Analytical Laboratory organizational chart	3
Figure 2.	Sample analysis flowchart, NTN	13
Figure 3.	Sample analysis flowchart, AIRMoN-wet.....	14
Figure 4.	Sample processing and data flowchart, NTN	35
Figure 5.	Sample processing and data flowchart, AIRMoN-wet	41

List of Tables

Table 1.	Summary of Sample Codes Assigned to Wet-Side Deposition Samples (AIRMoN-wet).....	8
Table 2.	Summary of Sample Codes Assigned to Wet-Side Deposition Samples (NTN).....	9
Table 3.	CAL Instrumentation	11
Table 4.	CAL Analytical Methods.....	12
Table 5.	Historical Method Detection Limits (MDLs) for Precipitation Analysis	15
Table 6.	Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/NTN Precipitation, Wet-only Samples, 1998 - 2002	18
Table 7.	Ion Percent Difference (IPD).....	26
Table 8.	Conductance Percent Difference (IPD)	26

Acronyms and Abbreviations

ADORC	Acid Deposition and Oxidation Research Center
AIRMoN-wet	Atmospheric Integrated Research Monitoring Network-wet component
ANSI	American National Standards Institute
ASQC	American Society for Quality Control
ASTM	American Society for Testing and Materials
CAL	Central Analytical Laboratory
CFR	Code of Federal Regulations
CPD	Conductance Percent Difference
DI	Deionized
DMAS	Data Management and Assessment Subcommittee
DQOs	Data Quality Objectives
FOF	Field Observer Form (AIRMoN-wet)
FORF	Field Observer Report Form (NTN)
FR25	A synthetic rainwater solution formulated to approximate the 25 th percentile concentrations of the NADP/NTN
FR75	A synthetic rainwater solution formulated to approximate the 75 th percentile concentrations of the NADP/NTN
GMT	Greenwich Mean Time
HDPE	High-Density Polyethylene
IPD	Ion Percent Difference
ISWS	Illinois State Water Survey
LABNO	Laboratory Number
LOF	Laboratory Observation Form (AIRMoN-wet)
LORF	Laboratory Observation Report Form (NTN)
MDL	Method Detection Limit
MRL	Method Reporting Limit
NADP	National Atmospheric Deposition Program
NED	Network Equipment Depot
NILU	Norwegian Institute for Air Research
NOS	Network Operations Subcommittee

Acronyms and Abbreviations (concluded)

NRSP-3	National Research Support Project
NTN	National Trends Network
PO	Program Office
QA	Quality Assurance
QA/R-5	EPA Requirements for QA Project Plans
QAP	Quality Assurance Plan
QC	Quality Control
QCS	Quality Control Standard
QMP	Quality Management Plan
Site ID	Station identification code
SL	Screening Level
SOP	Standard Operating Procedure
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
USPS	U.S. Postal Service
WMO/GAW	World Meteorological Organization/Global Atmospheric Watch

A. Project Management

1.0 Purpose of Plan

The Quality Assurance Plan (QAP) for the National Atmospheric Deposition Program (NADP) Central Analytical Laboratory (CAL) provides guidelines for producing analytical data for which NADP data quality indicators are quantified. Sample collection and transport, sample processing and chemical analysis, data validation and verification, and final transfer of data to the Program Office (PO) all require established protocols to ensure data that meets the needs of the data user. The QAP defines these quality indicators and indicates how they are to be monitored and quantified. This QAP is designed to cover all aspects of sample processing, sample analysis, instrument calibration, internal QC checks, data handling, data screening, and final data processing prior to data transfer to the NADP PO. It will be reviewed annually and updated as needed.

The laboratory that provides site support, sample processing, chemical analysis, and data validation services for precipitation samples collected at the NADP/Atmospheric Integrated Research Monitoring Network-wet component (NADP/AIRMoN-wet) and the NADP/National Trends Network (NADP/NTN) sites must follow strict quality assurance (QA) and quality control (QC) procedures. The laboratory that has provided these services to the NADP/NTN and NADP/AIRMoN-wet is located at the Illinois State Water Survey (ISWS) in Champaign, Illinois. The laboratory, referred to as the CAL, has been analyzing NADP/NTN samples since the program's inception in 1978.

From March through September 1987, analytical services for approximately 10 percent of the NADP/NTN sites were transferred to Environmental Monitoring and Services, Incorporated, Camarillo, California. Since October 1, 1987, the CAL has performed all analytical services for NADP/NTN. Since October 1992, the CAL has performed all analytical services for the NADP/AIRMoN-wet sites. The number of sites for each network fluctuates from year to year, increasing and decreasing the sample load to the CAL.

Quality assurance for the analytical measurement process at the CAL is a multi-tiered program that includes bench-level QC, laboratory management-level QA, and participation in external QA monitoring efforts. The laboratory continually strives to improve the current methods and to find new instrumentation that will achieve lower detection limits, improve sample throughput, improve measurement precision, and reduce bias for analytical measurements. Documentation of these methods' characteristics is updated annually in the laboratory QA report. Standard Operating Procedures (SOPs) for all support activities are maintained and updated annually.

The NADP/CAL QAP follows the ISWS Quality Management Plan (QMP), the "umbrella" QA document that describes the processes and procedures for staff and management to follow in producing environmental data. It is patterned after a national consensus standard, American National Standards Institute/American Society for Quality Control (ANSI/ASQC) E4-1994, and U.S. Environmental Protection Agency (USEPA)

Requirements for QA Project Plans (QA/R-5), a USEPA guidance document developed to assist each agency contractor in developing an agency-specific QAP.

The following is a list of relevant source documents:

- ISWS Quality Management Plan
- NADP Quality Management Plan
- NADP QA Plan
- AIRMoN-wet QAP
- CAL SOPs
- CAL Statement of Work

The CAL QA Specialist and the CAL Director review and update this plan annually. All revisions will be numbered and dated; previous versions will be kept in the CAL archives for reference.

2.0 Management and Organization

Several administrative levels are necessary for the management of the NTN and AIRMoN-wet site support, sample analysis, and data handling. The principal investigator for NADP is the NADP Program Coordinator who reports directly to the ISWS Chief and is also responsible to the NADP Executive Committee. The NADP CAL Director/Assistant Coordinator reports to the NADP Coordinator and is responsible for seeing that all laboratory activities follow the requirements defined in the CAL Statement of Work. Figure 1 shows a current organizational chart for the NADP CAL.

The QA Specialist for the NADP CAL is responsible for monitoring the overall quality of the laboratory. The QA Specialist performs QA/QC duties as assigned by the CAL Director. This QAP outlines specifics of these duties. Annually, the QA Specialist writes and presents the NADP Network Operations Subcommittee (NOS) with a detailed QA report summarizing QA/QC activities for the preceding year.

Principal investigators are the managers responsible for overseeing research and data collection activities funded from external sources. The NADP is a cooperative research support program of the State Agricultural Experiment Stations National Research Support Project (NRSP-3), federal and state agencies, private research organizations, and the University of Illinois.

The NADP technical staff includes scientists, permanent support staff, and hourly staff. The NADP staff are committed to QA and quality improvement of the network. As part of their routine responsibilities, the staff read and follow the CAL QAP, maintain and adhere to SOPs, and participate in improving the overall quality of the CAL.

NADP/CAL Organization

April 14, 2006

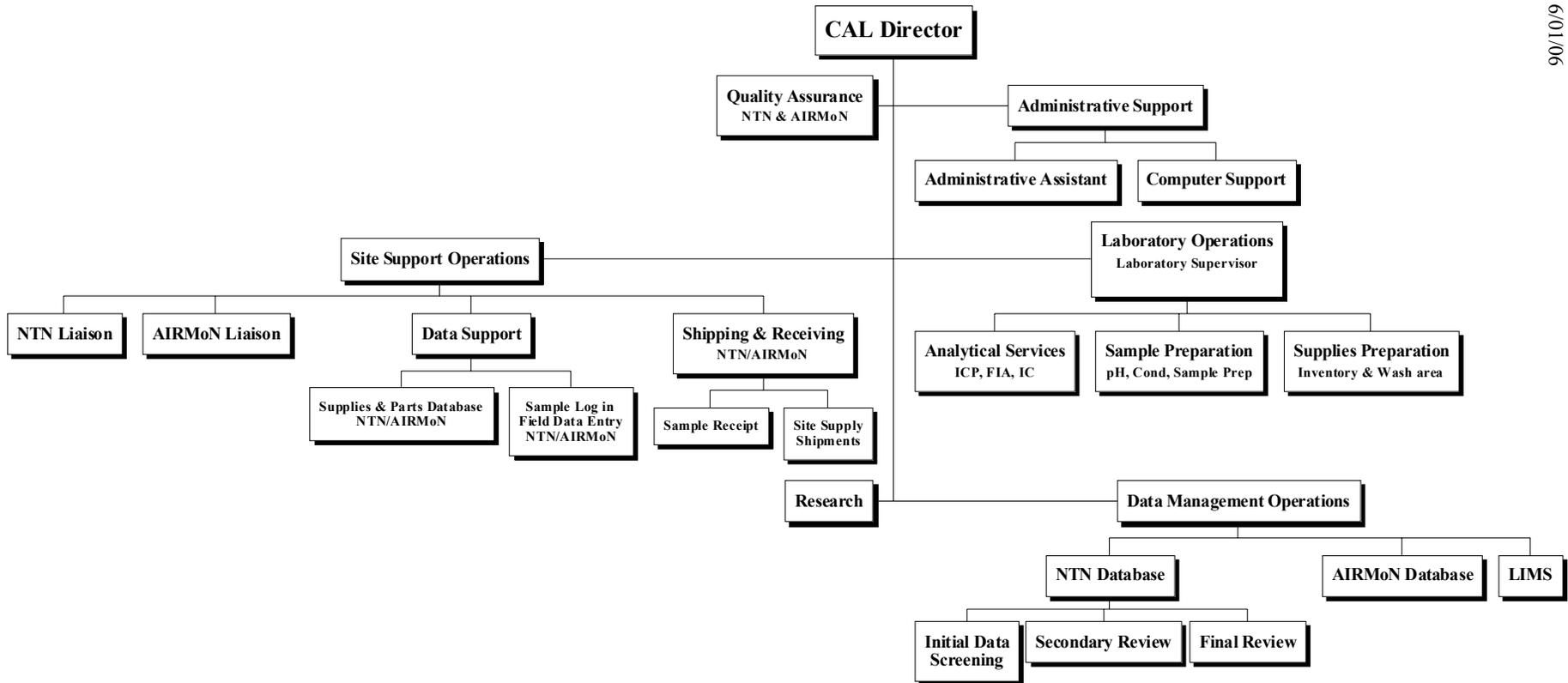


Figure 1. Central Analytical Laboratory organizational chart

3.0 Elements of NADP CAL Quality System

The QAP for the CAL describes the day-to-day QA/QC procedures used throughout the CAL. The CAL QA Specialist is responsible for maintaining the CAL QAP, which is modeled after the ISWS QMP and the USEPA QA/R-5.

Standard Operating Procedures (SOPs) are written documents that describe the detailed method for an operation, activity, or analysis so that the procedure can be consistently reproduced over a long time period. Appendix A of this document contains a list of the active SOPs for the CAL and covers all details of CAL operations from sample receipt to data transfer to the PO.

Periodic on-site technical reviews, conducted during the course of a project, are documented assessments of project work. They are used to evaluate documents, activities, materials, data, or other work products that require technical verification for bias, precision, completeness, or representativeness. The NADP Technical Committee, under the guidance of the NOS, DMAS, and the NADP QA Manager, conducts on-site CAL audits every three years with a follow-up paper review of the on-site audit one year following the on-site review. Internal ISWS technical reviews may be conducted by ISWS staff with equivalent experience and training in the project discipline. These reviews may be requested at any time by the NADP Program Coordinator, CAL Director, or QA Specialist. The CAL Director is responsible for retaining records that document review findings and responses.

4.0 Personnel Qualifications and Training

Functions performed by CAL staff require different educational backgrounds. The specific requirements for each job are listed in the SOP for that task. All chemical measurements are performed by analysts who have at least a Bachelor of Science degree in a physical or life sciences discipline or who are under the direct supervision of a degreed scientific staff member.

As a minimum requirement, new staff must be trained for specific jobs by another CAL staff member familiar with that job and may need to attend structured courses that cover specific training in instrumentation, procedures, or other areas of specialized need. Analytical staff must be proficient in the operation of each instrument as proven by analysis of blind samples for which the chemistry is known to the QA Specialist but not to the analyst. Only when the analysis of the blind samples is completed within specific control limits is the new analyst allowed to begin routine analysis of NADP precipitation samples.

Training for CAL analytical and data staff is ongoing. Staff are required to continually upgrade and expand their skills into new areas. Personal and professional development courses offered by the ISWS staff development program through the University of Illinois Office of Human Resources Development are available to all ISWS and CAL staff. Staff safety training also is provided through the University of Illinois Division of

Research Safety and the Illinois Department of Natural Resources. All NADP CAL staff are encouraged to participate in all safety training courses.

All NADP CAL staff must annually update resumes that include any courses taken during the year. These resumes are kept on file by the CAL Director and by ISWS Financial and Human Resources.

5.0 Laboratory Facilities

The NADP CAL facilities are located at the ISWS on the campus of the University of Illinois at Urbana-Champaign. Total square footage for laboratories at the CAL is approximately 1772 ft².

B. Laboratory Operations

1.0 Program Objectives

Program objectives include chemical analyses of wet deposition samples and recording, verifying, screening, and reporting data. Integral parts of this program are QC of the sample analyses and QA of the data review and transfer.

2.0 Sample Processing

Detailed information on processing for both NADP/NTN and NADP/AIRMoN-wet is contained in SOPs for sample preparation (see Appendix A for current list of SOPs).

As samples are logged in, information from the Field Observer Report Form (FORF) or Field Observer Form (FOF) is entered into a computer data file. Each sample is identified by sample number (LABNO) and station identification code (Site ID).

Samples are assigned an alphanumeric designation that includes the type of sample and a unique sequential laboratory number for ease of identification. Only this number is used when recording the chemical analyses.

Sample processing differs for AIRMoN-wet and NTN.

- Sample processing protocols are dependent upon sample volume. Different protocols are used for AIRMoN-wet and NTN (see Tables 1 and 2, respectively, for details.)
- Both pH and specific conductance must be measured for all samples within a week of their arrival at the CAL (AIRMoN-wet samples) and within 72 hours of sample login (NTN samples).
- All other analyses must be completed within two weeks of their arrival at the CAL (AIRMoN-wet samples) and within three weeks of their arrival at the CAL (NTN samples).
- The order for chemical analysis of AIRMoN-wet samples is 1) pH and conductivity, with pH taking precedence when there is insufficient sample for both analyses, 2) flow injection analysis for ammonium and orthophosphate, 3) ion chromatographic analysis of chloride, nitrate, and sulfate, and 4) inductively coupled plasma-optical emission spectroscopic analysis of magnesium, calcium, sodium, and potassium. The order for chemical analyses of NTN samples is pH and conductivity, and the order of remaining analyses is not prioritized.

3.0 Site Resupply

The NADP ongoing long-term monitoring program requires specific equipment and established protocols to maintain data consistency throughout the networks. The CAL

Table 1. Summary of Sample Codes Assigned to Wet-Side Deposition Samples (AIRMoN-wet)

<i>Type</i>	<i>Sample volume (Vol)</i>	<i>Prioritization of chemical measurements</i>
WI	10 mL ≤ Vol < 50 mL	As volume permits: pH and conductance; NH ₄ ⁺ and PO ₄ ³⁻ ; Cl ⁻ , NO ₃ ⁻ , and SO ₄ ²⁻ ; and Ca ²⁺ , Mg ²⁺ , Na ⁺ , and K ⁺ until there is no more sample. If all components are measured the sample is a 'W' (see below).
W	Vol ≥ 50 mL	Start with pH and conductance; NH ₄ ⁺ , PO ₄ ³⁻ , Cl ⁻ , NO ₃ ⁻ , SO ₄ ²⁻ , Ca ²⁺ , Mg ²⁺ , Na ⁺ , and K ⁺ in that order.
DF	Field Blank - bucket component	Field Blank bottle sent from the CAL: half is poured into the bucket then, after about 8 hours, is poured into a clean bottle and returned to the CAL for analysis as if it were a 'W' (see above).
DK	Field Blank - bottle component	Half of the Field Blank bottle, not poured into the sample bucket, is returned to the CAL in the original bottle, and analyzed as if it were a 'W' (see above).
D	0 mL ≤ Vol < 10 mL	No sample shipped.

Table 2. Summary of Sample Codes Assigned to Wet-Side Deposition Samples (NTN)

<i>Type</i>	<i>Sample volume (Vol)</i>	<i>Prioritization of chemical measurements</i>
T	Vol \leq 10 mL	As volume permits: first pH and then conductance on unfiltered sample.
WD	10 mL < Vol < 35 mL	pH and conductance on unfiltered aliquot; all other ions on filtered sample after dilution to a volume of 50 mL with deionized water to provide adequate sample for analyses; measured concentrations are subsequently corrected for dilution.
W	Vol \geq 35 mL	pH and conductance on unfiltered aliquot; all other ions on filtered aliquot.
D	Vol = 0 mL	No analysis is performed.
DF	Field Blank - bucket component	USGS Field Blank bottle sent from the site 75% is poured into the bucket then, after about 24 hours, is poured into a clean sample bottle and returned to the CAL for analysis as if it were a 'W' (see above).
DK	Field Blank - bottle component	25% of the USGS Field Blank bottle, not poured into the sample bucket, is returned to the CAL in the original bottle, and analyzed as if it were a 'W' (see above).

must supply materials of identical quality to those being replaced at the sites. The laboratory provides supplies and solutions for both NTN and AIRMoN-wet. For more detailed information, see SOPs relating to supplies preparation (see Appendix A for current list of SOPs).

4.0 Sample Chemical Analysis

Table 3 lists the parameters to be measured, instruments used, and the dates the instruments were purchased. Table 4 lists the analytical methods. See Appendix A for a complete listing of analytical SOPs. Figure 2 is a flowchart for processing NTN samples. Figure 3 is a flowchart for processing AIRMoN-wet samples.

Quality assurance for analytical measurements is a multi-tiered program that includes bench-level QC, laboratory management-level QA, and external QA monitoring. The overall program objective is to produce analytical data for which precision and bias are quantified. DQOs are defined to maximize data quality.

Method Detection Limits (MDLs) are the minimum concentration of an analyte that can be reported with a 99 percent confidence that the value exceeds zero. The MDL is based on a standard deviation of greater than seven replicate measurements of the analyte in the matrix of concern at a concentration near the low standard (Code of Federal Regulations, Part 136, Vol.49, No. 209, Appendix B). The MDLs are a data quality indicator that is reviewed and recalibrated by the QA Specialist as warranted, i.e., when a new instrument is purchased, when a critical new part is installed on an existing instrument, or for new analysts using the instruments. The MDLs are also calculated at least annually using one of the internal blind samples processed every two weeks through the laboratory. The results are compiled from the previous 12 months data and reviewed by the QA Specialist for recommended changes. The solution used is a simulated precipitation sample approximating the tenth percentile concentration of the analytes measured by the CAL for NADP, which complies with the Code of Federal Regulations in that the concentrations of the analytes are approximately ten times the MDL of each analyte. Since these samples are processed through the laboratory in the same manner as real samples and are blind to the analysts, the MDL generated from these solutions is an excellent representative of the true laboratory MDL for each analyte. The only analyte not included in the simulated rain solution is orthophosphate. A separate solution is used biweekly to calculate the orthophosphate detection limit. Table 5 lists some of the historical MDLs for the CAL.

Bias, as defined in the ISWS Quality Management Plan, is a persistent positive or negative deviation of the measured value from the true value. Bias for NTN and AIRMoN-wet is determined by the analysis of routine blind samples of known concentration.

The bias goals will depend on the concentration of the analyte (NADP QAP, 1993):

- A maximum allowable bias of ± 100 percent at the MDL.
- A ± 20 percent allowable bias at 10 times the MDL.
- A ± 10 percent allowable bias at 100 times or greater the MDL.

Table 3. CAL Instrumentation

<i>Type of Equipment</i>	<i>Model</i>	<i>Purchased</i>	<i>Analytes</i>
Ion chromatography, conductivity detection	2 Dionex Model DX-500 2 Dionex Model ICS-2000	December 1994 April 2004	Cl ⁻ NO ₃ ⁻ SO ₄ ²⁻
Flow injection analyzer	Lachat Instruments Quick Chem 8000	October 1996	NH ₄ ⁺ PO ₄ ³⁻
Inductively coupled plasma spectrophotometer	Varian, Vista-Pro	January 2004	Na ⁺ K ⁺ Mg ²⁺ Ca ²⁺
pH meter pH meter	Corning 445 Corning 445	June 1998 April 2000	pH pH
Conductivity meter	YSI 3200	August 2000	Specific conductance
Conductivity meter	YSI 3200	April 2003	Specific conductance

Table 4. CAL Analytical Methods

Calcium, Magnesium, Sodium, and Potassium

Illinois State Water Survey, NADP CAL SOP ICP-01, The Determination of Calcium, Magnesium, Sodium, Potassium by Inductively Coupled Plasma-Optical Emission Spectroscopy

Ammonium

Illinois State Water Survey, NADP CAL SOP FIA-01, The Determination of Ammonium (phenolate) by Flow Injection Analysis.

Orthophosphate

Illinois State Water Survey, NADP CAL SOP FIA-02, The Determination of Orthophosphate by Flow Injection Analysis.

Chloride, Nitrate, and Sulfate

Illinois State Water Survey, NADP CAL SOP IC-01, The Determination of Cl, NO₃, and SO₄ using Dionex DX-500 Ion Chromatographs.

Chloride, Nitrate, and Sulfate

Illinois State Water Survey, NADP CAL SOP IC-02, The Determination of Cl, NO₃, and SO₄ using Dionex ICS-2000 Ion Chromatographs.

ASTM Method D5085, Standard Test Method for Determination of Chloride, Nitrate, and Sulfate in Atmospheric Wet Deposition by Chemically Suppressed Ion Chromatography, *Annual Book of ASTM Standards*, Section 11, Vol. 11.03, pp. 389-397, 2003.

pH

Illinois State Water Survey, NADP CAL SOP, PH-01, The Determination of pH.

ASTM Method D5015, Standard Test Method for pH of Atmospheric Wet Deposition by Electrometric Determination, *Annual Book of ASTM Standards*, Section 11, Vol. 11.03, pp. 375-380, 2003.

Conductivity

Illinois State Water Survey, NADP CAL SOP COND-01, The Determination of Conductivity.

Other

ASTM Method D5012, Standard Guide for Preparation of Materials Used for the Collection and Preservation of Atmospheric Wet Deposition, *Annual Book of ASTM Standards*, Section 11, Vol. 11.03, pp. 363-367, 2003.

ASTM Method D6328, Standard Guide for Quality Assurance Protocols for Chemical Analysis of Atmospheric Wet Deposition, *Annual Book of ASTM Standards*, Section 11, Vol. 11.03, pp. 839-844, 2003.

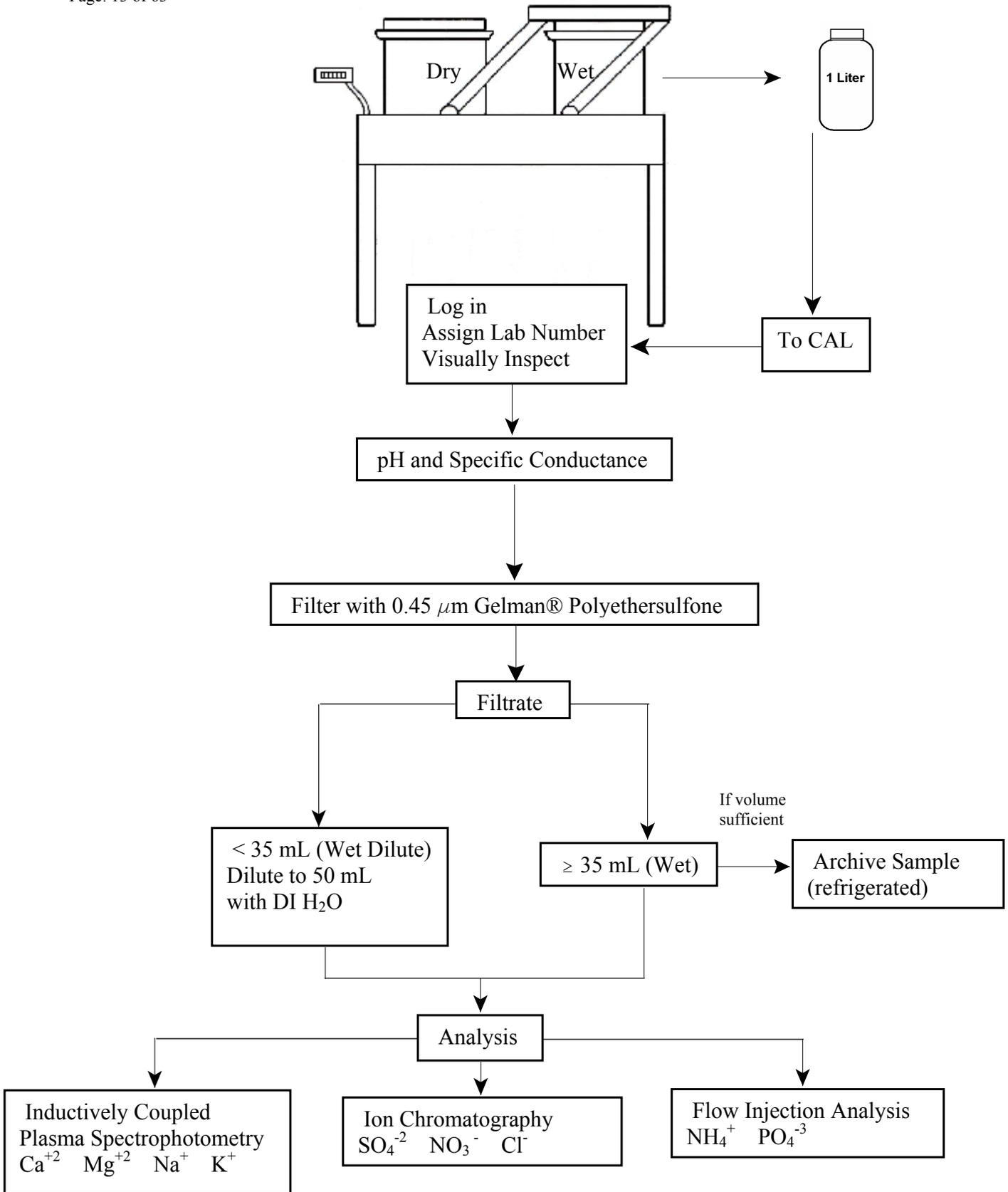


Figure 2. Sample analysis flowchart, NTN

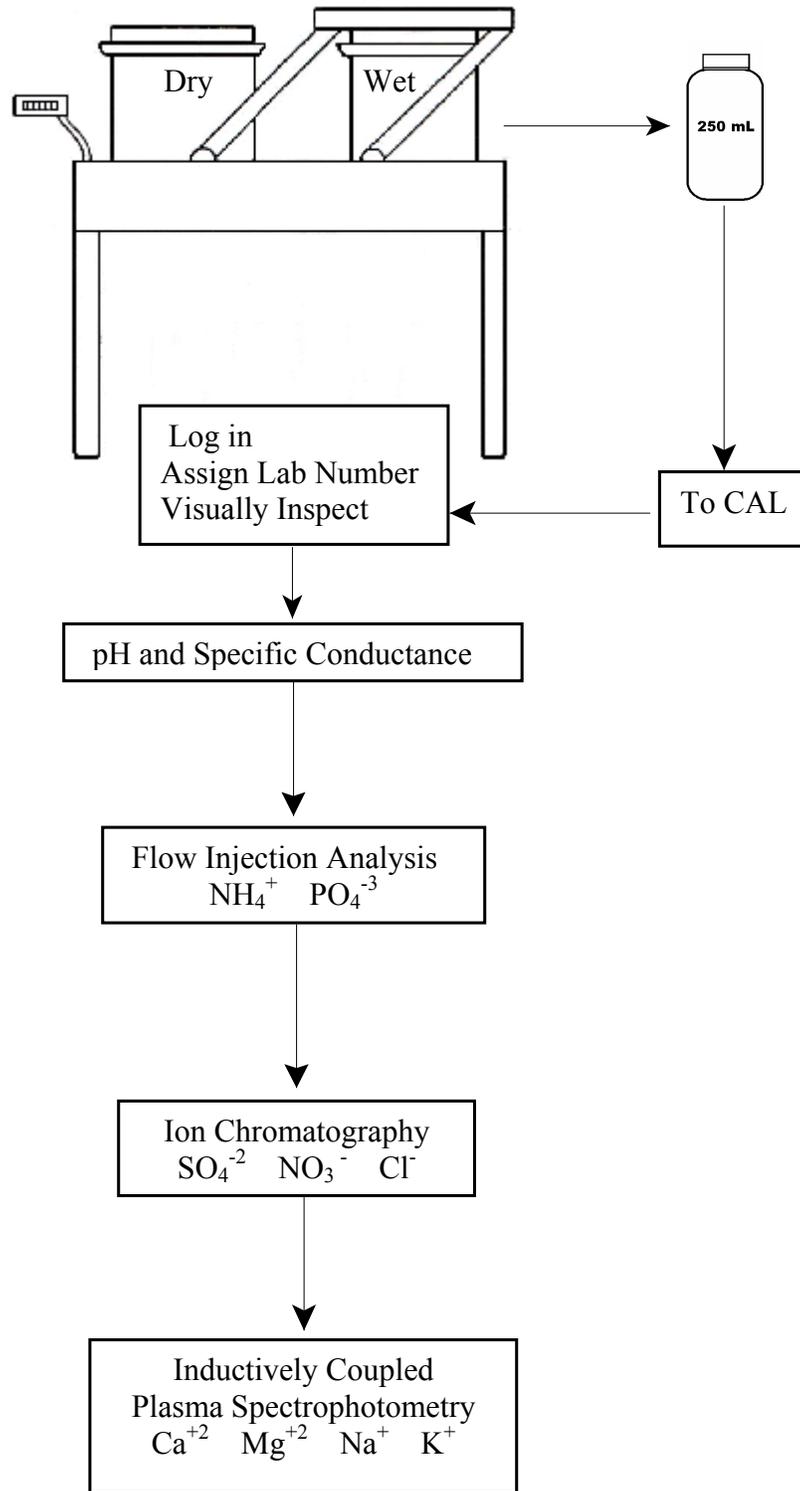


Figure 3. Sample analysis flowchart, AIRMoN-wet

Table 5. Historical Method Detection Limits (MDLs) for Precipitation Analysis

<i>Analyte</i>	<i>Field Sampling Dates</i>	<i>Lab ID Sequence (LABNO)</i>	<i>Method Detection Limit (MDL) (mg/L)</i>	<i>Analytical Methodology</i>
Calcium	Jul 78 - Dec 78	NA0001 - NA0221	0.01	Flame Atomic Absorption Spectrophotometry
	Dec 78 - Jan 79	NA0222 - NA0335	0.02	Flame Atomic Absorption Spectrophotometry
	Jan 79 - Apr 79	NA0336 - NA0668	0.01	Flame Atomic Absorption Spectrophotometry
	Apr 79 - Aug 80	NA0669 - NA3361	0.02	Flame Atomic Absorption Spectrophotometry
	Aug 80 - Sep 80	NA3362 - NA3695	0.008	Flame Atomic Absorption Spectrophotometry
	Sep 80 - Oct 80	NA3696 - NA4254	0.006	Flame Atomic Absorption Spectrophotometry
	Oct 80 - Apr 81	NA4255 - NA6328	0.008	Flame Atomic Absorption Spectrophotometry
	Apr 81 - May 81	NA6329 - NA6543	0.024	Flame Atomic Absorption Spectrophotometry
	May 81 - Dec 03	NA6544 - NY6346	0.009	Flame Atomic Absorption Spectrophotometry
	Jan 04 - Dec 04	NY6347 - TA0214	0.009	Inductively Coupled Plasma
Jan 05 - Dec 05	TA0215 - TB4169	0.002	Inductively Coupled Plasma	
Magnesium	Jul 78 - Apr 81	NA0001 - NA6328	0.002	Flame Atomic Absorption Spectrophotometry
	Apr 81 - May 81	NA6329 - NA6543	0.009	Flame Atomic Absorption Spectrophotometry
	May 81 - Jul 81	NA6544 - NA7299	0.002	Flame Atomic Absorption Spectrophotometry
	Jul 81 - Dec 03	NA7300 - NY6346	0.003	Flame Atomic Absorption Spectrophotometry
	Jan 04 - Dec 04	NY6347 - TA0214	0.003	Inductively Coupled Plasma
	Jan 05 - Dec 05	TA0215 - TB4169	0.001	Inductively Coupled Plasma
Sodium	Jul 78 - Aug 80	NA0001 - NA3475	0.004	Flame Atomic Absorption Spectrophotometry
	Aug 80 - Aug 81	NA3476 - NA7741	0.002	Flame Atomic Absorption Spectrophotometry
	Aug 81 - Dec 03	NA7742 - NY6346	0.003	Flame Atomic Absorption Spectrophotometry
	Jan 04 - Dec 05	NY6347 - TB4169	0.003	Inductively Coupled Plasma
Potassium	Jul 78 - Jan 79	NA0001 - NA0335	0.002	Flame Atomic Absorption Spectrophotometry
	Jan 79 - Feb 79	NA0336 - NA0446	0.004	Flame Atomic Absorption Spectrophotometry
	Feb 79 - Sep 79	NA0447 - NA1331	0.002	Flame Atomic Absorption Spectrophotometry
	Sep 79 - Nov 79	NA1332 - NA1675	0.004	Flame Atomic Absorption Spectrophotometry
	Nov 79 - Dec 79	NA1676 - NA1800	0.002	Flame Atomic Absorption Spectrophotometry
	Dec 79 - Aug 80	NA1801 - NA3475	0.004	Flame Atomic Absorption Spectrophotometry
	Aug 80 - Apr 81	NA3476 - NA6000	0.002	Flame Atomic Absorption Spectrophotometry
	Apr 81 - Dec 03	NA6001 - NY6346	0.003	Flame Atomic Absorption Spectrophotometry
	Jan 04 - Dec 04	NY6347 - TA0214	0.003	Inductively Coupled Plasma
	Jan 05 - Dec 05	TA0215 - TB4169	0.001	Inductively Coupled Plasma

Table 5 (concluded)

Analyte	Field Sampling Dates	Lab ID Sequence (LABNO)	Method Detection Limit (MDL) (mg/L)	Analytical Methodology
Ammonium	Jul 78 - Oct 78	NA0001 - NA0104	0.03	Phenate (Segmented Flow Colorimetry)
	Oct 78 - Apr 81	NA0105 - NA6000	0.02	Phenate (Segmented Flow Colorimetry)
	Apr 81 - May 81	NA6001 - NA6650	0.01	Phenate (Segmented Flow Colorimetry)
	May 81 - Jun 89	NA6651 - NH6700	0.02	Phenate (Segmented Flow Colorimetry)
	Jun 89 - Dec 04	NH6701 - TA0334	0.02	Phenate (Flow Injection Colorimetry)
	Jan 05 - Dec 05	TA0335 - TB4169	0.005	Phenate (Flow Injection Colorimetry)
Chloride	July 78 - Apr 81	NA0001 - NA6000 ¹	0.05	Ferricyanide (Segmented Flow Colorimetry)
	Apr 81 - Apr 85	NA6001 - ND1937	0.02	Ion Chromatography
	Apr 85 - Dec 99	ND1938 - NS3700	0.03	Ion Chromatography
	Jan 00 - Dec 04	NS3701 - NZ9957	0.005	Ion Chromatography
	Jan 05 - Dec 05	NZ9958 - TB4169	0.008	Ion Chromatography
Nitrate + Nitrite	Jul 78 - Oct 78	NA0001 - NA0080	0.03	Cadmium Reduction (Segmented Flow Colorimetry)
	Oct 78 - Apr 85	NA0081 - ND1938	0.02	
Nitrate	Apr 85 - Dec 99	ND1939 - NS3700	0.03	Ion Chromatography
	Jan 00 - Dec 04	NS3701 - NZ9957	0.010	Ion Chromatography
	Jan 05 - Dec 05	NZ9958 - TB4169	0.009	Ion Chromatography
Sulfate	Jul 78 - Apr 85	NA0001 - ND1938 ²	0.10	Methylthymol Blue (Segmented Flow Colorimetry)
	Apr 85 - Dec 99	ND1939 - NS3700	0.03	Ion Chromatography
	Jan 00 - Dec 04	NS3701 - NZ9957	0.010	Ion Chromatography
	Jan 05 - Dec 05	NZ9958 - TB4169	0.013	Ion Chromatography
Orthophosphate	Jul 78 - Oct 78	NA0001 - NA0067	0.005	Ascorbic Acid Reduction (Segmented Flow Colorimetry)
	Oct 78 - Feb 79	NA0068 - NA0452	0.004	Ascorbic Acid Reduction (Segmented Flow Colorimetry)
	Feb 79 - Apr 85	NA0453 - ND2633	0.003	Ascorbic Acid Reduction (Segmented Flow Colorimetry)
	Apr 85 - Jun 87	ND2634 - NF4630 ³	0.01	Ascorbic Acid Reduction (Segmented Flow Colorimetry)
	Jun 87 - Nov 93	NF4631 - NM6824 ⁴	0.02	Ion Chromatography
	Nov 93 - Dec 00	NM6825 - NU7201	0.003	Ascorbic Acid Reduction (Flow Injection Colorimetry)
	Jan 01 - Dec 04	NU7202 - NW0218	0.009	Ascorbic Acid Reduction (Flow Injection Colorimetry)
	Jan 05 - Dec 05	NW0219 - TB4169	0.006	Ascorbic Acid Reduction (Flow Injection Colorimetry)

Notes:

¹ Sample NA5766 had a detection limit of 0.020 mg Cl/L.

² Sample NB1415 had a detection limit of 0.06 mg SO₄²⁻/L, and samples NB2015 and NB2254 had detection limits of 0.05 mg SO₄²⁻/L.

³ Samples NF4532Q and NF4558Q had detection limits less than 0.020 mg PO₄³⁻/L.

⁴ Sample NM6394 had a detection limit of 0.006 mg PO₄³⁻/L, sample NM6764Q had a detection limit of 0.009 mg PO₄³⁻/L, and sample NM6816Q had a detection limit of less than 0.003 mg PO₄³⁻/L.

The allowable bias and precision for the pH and specific conductance of a sample are:

- Samples with pH less than 5.0 pH units, ± 0.1 pH units allowable bias and ± 0.03 pH units allowable precision.
- Samples with pH greater than 5.0 pH units, ± 0.3 pH units allowable bias and ± 0.1 pH units allowable precision.
- Samples with specific conductance of 10-100 $\mu\text{S}/\text{cm}$, ± 10 percent allowable bias and ± 3 percent allowable precision.
- Samples with specific conductance of greater than 100 $\mu\text{S}/\text{cm}$, ± 6 percent allowable bias and ± 2 percent allowable precision.

The difference allowed between the original sample analysis and split samples or randomly selected reanalyzed samples is 10 percent. Any reanalysis sample with a greater than 10 percent difference must be reanalyzed to ascertain which concentration is correct unless it is clear the sample chemistry is changing.

Standardization is instrument specific. All instruments are standardized each day they are used. In addition, pH and specific conductance are standardized every 36 samples. A minimum of five standards is used to standardize the inductively coupled plasma-optical emission spectroscopy (ICP), flow injection colorimetry (FIA), and ion chromatography (IC). The standard levels used are based on approximately the 5th percentile to the 99th percentile concentrations found in the NADP/NTN data set (Table 6). For some analytes, however, this range is too broad, resulting in the higher concentrations not being within the dynamic range of the instrument. For these analytes, a lower than 99th percentile standard, one that is within the instruments dynamic range, must be used for the highest standards. Where possible, the highest standard for each analyte is near the 99th percentile concentration. All analytes with concentrations exceeding the highest standard must be diluted and analyzed in the diluted form. This results in typically less than 1 percent of the samples requiring dilution.

Standardization and calibration procedures are the same for AIRMoN-wet and NTN.

All primary standards must be confirmed using these two methods:

- Certified reference solutions or second source standards to compare with the new stock standards.
- Prior standards to compare with the new standards.

If other comparisons are done instead of the above two, they must be approved by the QA Specialist and documented in the laboratory log book and the SOP for that method. All primary standard solutions are remade or purchased on or before the expiration date of the old solutions. Instrument standardization procedures are documented for each analyte (see Appendix A for appropriate SOPs). The frequency of standardization may vary with the measurement but is not less than once per analysis day.

Table 6. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/NTN Precipitation Wet-only Samples, 1998 – 2002

<i>Parameter</i>	<i>Minimum</i>	<i>Percentile Concentration Values (mg/L)</i>								<i>Maximum</i>
		<i>5th</i>	<i>10th</i>	<i>25th</i>	<i>50th</i>	<i>75th</i>	<i>90th</i>	<i>95th</i>	<i>99th</i>	
Calcium	MDL	0.017	0.0264	0.053	0.118	0.267	0.544	0.807	1.905	61.680
Magnesium	MDL	0.003	0.005	0.010	0.022	0.046	0.090	0.143	0.290	3.880
Sodium	MDL	0.006	0.009	0.019	0.049	0.141	0.400	0.699	2.250	33.200
Potassium	MDL	MDL	0.004	0.009	0.018	0.038	0.074	0.108	0.292	6.080
Ammonium	MDL	MDL	0.03	0.09	0.23	0.46	0.77	1.04	1.79	16.93
Sulfate	MDL	0.136	0.230	0.530	1.070	1.913	3.050	4.000	6.265	125.480
Nitrate	MDL	0.175	0.293	0.598	1.120	1.920	2.940	3.771	6.203	45.430
Chloride	MDL	0.022	0.030	0.052	0.108	0.249	0.663	1.225	3.724	35.000
Orthophosphate	MDL	MDL	MDL	MDL	MDL	MDL	MDL	MDL	0.030	8.703
pH (units)	3.41	4.16	4.28	4.50	4.86	5.34	5.96	6.32	6.79	8.12
Conductivity (µS/cm)	1.1	3.4	4.5	7.5	12.9	21.6	33.6	42.1	68.7	464.0

Notes: Number of samples = 39,602. Mean sample volume = 1487.5 mL. Median sample volume = 909.08 mL.

5.0 Record Archives

All CAL log books are permanently kept in the laboratories. Digital analytical records are maintained for five years following date of analysis. Paper records for analyses not digitally saved must be retained for five years following date of analysis. For analytical methods with digital records and paper records, the paper records must be maintained for 2.5 years after date of analysis.

6.0 General Laboratory Procedures

Precipitation samples are typically characterized by a low dissolved solids content (< 20 mg/L) resulting in a highly unbuffered system. Because of this, a QA program for the chemical analysis of precipitation samples requires stringent laboratory conditions and careful control over all aspects of the analyses.

All new sources of laboratory glass and plasticware are evaluated prior to use to ensure that ions of interest are neither adsorbed to nor leached from the surfaces in contact with the sample.

High density polyethylene (HDPE) bottles are used for sample storage.

Borosilicate glass or HDPE containers are used for standard solution preparation and storage.

- All volumetric glassware is Class A under American Society for Testing and Materials (ASTM) Standards E287 for Burets, E288 for Volumetric Flasks, and E969 for Volumetric (transfer) Pipettes (*Annual Book of ASTM Standards*, Vol. 14.02).
- The bias and precision of pipettors used is determined following the ISWS SOP for pipettor performance verification (SOP ISWS-1).
- Deionized water used for solution preparation must have a resistivity of greater than or equal to 18 Mohms-cm, or ASTM Type I water (ASTM Standard Specification for Reagent Water, D1193, *Annual Book of ASTM Standards*, Vol. 11.01).

Polyethersulfone filters separate the dissolved and suspended fractions found in precipitation for the NTN samples.

- Whenever a new lot of filters is obtained, the filters are checked by passing a synthetic precipitation sample that approximates the 25th percentile concentration level for NADP/NTN samples (FR25) and DI water through them to check for sorption and/or leaching contaminants.
- The solutions are analyzed, and approved by the QA Specialist providing the concentrations of the leachates are within established control limits.

- Before a new analyst can filter samples, his/her performance will be assessed and validated by monitoring QC samples to check his/her filtering technique.
- If the concentrations of the solutions used are within the standard control limits for those solutions, the QA Specialist approves the use of the new lot of filters or approves the performance of the new analyst.

7.0 Instrument Procedures

A high and a low quality control standard (QCS) are analyzed immediately after standardization to ensure that the system is functioning properly.

At a frequency of not less than one sample in 12, a QCS, duplicate, single-point standard having a concentration within the working range of the procedure, or any combination of the three solutions is analyzed to verify the system is in control.

All QC data is recorded directly from the analytical instruments into the LIMS.

Control charts of the data are automatically generated in the LIMS as soon as data transfer is complete. Analysts use the control charts to help determine if their analytical systems are in control.

The analytical and pan balances are monitored for proper operation and accuracy by using National Institute for Standards and Technology Traceable Class S weights on a monthly basis. Analytical balances are serviced yearly or when test weight values are not within the manufacturer's instrument specifications, whichever occurs first.

8.0 Analytical Blanks

Collection buckets and lids are cleaned and individually wrapped at the CAL.

Two percent of the cleaned buckets are checked for contamination.

- Three buckets per week receive 50 mL treatments, two with deionized (DI) water and one with FR25.
- Two buckets per week also receive 150 mL treatments with DI water and FR25, respectively.

Two snap-on lids per week are leached to ascertain the efficacy of the cleaning procedure using 50 mL DI water and 50 mL of FR25, respectively.

The CAL cleans shipping bottles for both NTN and AIRMoN-wet and stores them in Ziploc® bags. Cleanliness is checked in four 1-L NTN bottles weekly and two AIRMoN-wet 250-mL bottles monthly.

- The two AIRMoN-wet bottle blanks checked include 50 mL of FR25 and 150 mL of FR25, respectively.

- The four NTN bottle blanks checked include 50 mL of FR25, 150 mL of FR25, 50 mL of DI water, and 150 mL of DI water, respectively.

Each week 50 mL of DI water is poured into clean 60-mL HDPE bottles for DI water blanks. Each week a DI water sample is collected and analyzed from the sample preparation laboratory, the analytical laboratory, and the wash area.

Two filter blanks are analyzed each week.

- One filter is precleaned with 250 mL DI water and leached with 50 mL DI water.
- One filter is precleaned with 250 mL DI water and leached with 50 mL FR25.

Two plastic bag blanks (bags used for bucket and lid storage) are analyzed each week.

- One bag is leached with 50 mL DI water.
- One bag is leached with 50 mL FR25.

All solutions in the buckets and bottles are in contact with their containers for one week before being decanted into 60-mL HDPE bottles for analysis.

All lid blanks are kept in contact with the lids for four to five hours before being decanted into cleaned 60-mL HDPE analysis bottles.

If two or more concentration values for any blank solution exceed the NADP/NTN historical 10th percentile levels for the analyte (only 10 percent of all of the precipitation samples collected for NADP/NTN contain less of the analyte of interest), more blank solutions are analyzed to determine if the values in question are random or persistent, and to investigate and eliminate the cause of high values.

9.0 Sample Precision

Replicate analysis is performed on approximately 2 percent of the NADP/AIRMoN-wet and 1 percent of the NADP/NTN samples. Samples of sufficient volume are split at the CAL, and the bottles are separated by 60 to 100 sample identification numbers so that the analyses are separated over time. Replicates are given unique identification numbers and are blind to the analysts.

Internal QC samples are used to monitor the analytical procedures. Four QC samples, one per week, are introduced into the analytical queue each month disguised as real precipitation samples for AIRMoN-wet and three samples per week for NTN.

- The AIRMoN-wet blinds are double blinds: blind to the sample receiving personnel (samples appear as real precipitation samples) and blind to the analysts (concentrations are unknown and the bottles containing the samples are not known to be QC samples). The AIRMoN-wet samples can be of any

concentration as long as they appear to be normal precipitation samples to the analysts.

- The NTN samples are double blind to all analysts except those doing pH and conductivity analyses. For NTN, four different solutions are rotated through the laboratory on a prescribed schedule: low concentration synthetic rain obtained from a commercial source, high concentration synthetic rain prepared in-house, DI water from room 302, and a low ionic strength synthetic rain sample prepared in-house.

Two solutions each week, one or two of the synthetic rain samples and/or the DI water are poured into 60-mL HDPE analysis bottles. Samples are not filtered. The site identification code for these samples is SWS1 (high or low synthetic rain) and SWS2 (DI water or low ionic strength synthetic rain sample).

The third sample, SWS3, is the same solution as the SWS1 or SWS2 sample for that week, but is filtered before being poured into a 60-mL HDPE bottle for analysis.

Results of the measurements are compared with the target concentrations for each ion. Analytical bias is estimated from the mean differences between the measured and target values, and precision is estimated from the relative standard deviation of the measurements for each chemical matrix. The CAL QA Specialist reports results obtained from the blind samples for each network in the annual CAL QA report and summarizes and reviews the results monthly.

10.0 Sample Storage

All NADP/AIRMoN-wet samples must be stored at 4°C. These samples are kept at the CAL for two years after finalized data have been published by the PO.

For NADP/NTN, whenever there is sufficient sample for 120 mL to be filtered, 60 mL is filtered into a round bottle and used for analyses. These bottles are kept at ambient temperature until the data for those samples have been sent to the PO, then they are discarded. The second 60 mL is filtered into a square bottle and archived at 4°C. Archived samples from three sites (NH02, NE15, and IL11) and every 100th sample must be kept for the life of the program. All other archived samples must be stored for five years after data have been published by the PO. Samples can be discarded or sent to other researchers for independent studies after this time.

External intercomparison samples are stored at 4°C. All USGS intercomparison samples and blank samples are stored in the laboratories during processing. After completion of the analysis, the samples are stored in the NTN archive sample refrigerator until the QA specialist has reviewed the results of the USGS intercomparison samples after which these samples are discarded.

11.0 Data Verification

Chemical results for all analytes are captured directly by data acquisition software into the LIMS. Keyboard data entry is stroke-verified through double entry by a second person for all field forms (NTN and AIRMoN). For more information, see “Data Management Operations” (Section D).

Computer programs contain control checks for data entry. An ion percent difference is calculated for each sample (see Section C). The percentage difference between calculated and measured specific conductance is tabulated (see Section C). Samples are randomly selected for reanalysis for both AIRMoN-wet and NTN to verify sample concentrations (see Section C “Laboratory QA/QC Procedures” for more information).

12.0 Preventive Maintenance/Service

A maintenance schedule is established for each instrument. See SOPs for specifics. A record log of all scheduled and unscheduled maintenance is kept. The record log includes, at a minimum, the date, name of service provider, and nature of the service. The CAL Director and the CAL QA Specialist periodically review the record logs.

C. Laboratory QA/QC Procedures

1.0 Performance and Systems Audits

The CAL participates in several formal external QA programs.

The United States Geological Survey (USGS) operates the Interlaboratory Comparison Program for NADP/NTN.

- Laboratory intercomparison samples of four natural rainwater, deionized water, or reference samples are analyzed every two weeks.
- The USGS provides deionized water blanks to test for false positive values.

The CAL participates in other interlaboratory comparison programs such as those hosted by the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW), the Canadian Centre for Inland Waters (NWRI), and the Norwegian Institute for Air Research (NILU).

On-site reviews of the CAL are conducted every three years by the NADP. The NADP QA Manager selects the team in accordance with the NADP Quality Management Plan. The review team reports results of performance and system audits to NOS and the CAL Director. The CAL Director must respond to the NOS and NADP QA Manager within six months of the review. NADP/NOS also requires a paper review of the audit findings one year after the initial audit to ensure that critical corrective actions have been implemented.

Reanalysis of both NTN and AIRMoN-wet samples is dependent on the number processed. For NTN, one percent of the total number of samples analyzed during the month are randomly selected for reanalysis. For AIRMoN-wet, two percent of the samples are randomly selected for reanalysis. Samples also are selected for reanalysis if they exceed the predetermined control limits for ion balance and specific conductance differences. See Table 7 for the Ion Percent Difference (IPD) reanalysis criteria and Table 8 for the Conductance Percent Difference (CPD) reanalysis criteria. Approximately 2-6 percent of all samples are reanalyzed for NTN. Approximately 4-6 percent of all samples are reanalyzed for AIRMoN-wet.

Table 7. Ion Percent Difference (IPD)

$$\text{IPD} = \frac{(\text{Anions} - \text{Cations}) \times 100}{\text{Anions} + \text{Cations}}$$

Reanalyze if Anions + Cations < 50 µeq/L and IPD < -60% or IPD > +60%.

Reanalyze if Anions + Cations ≥ 50 µeq/L but <100 µeq/L and IPD < -30% or IPD > +30%.

Reanalyze if Anions + Cations ≥ 100 µeq/L and IPD < -15% or IPD > +15%.

Table 8. Conductance Percent Difference (CPD)

$$\text{CPD} = \frac{(\text{Calculated Conductance} - \text{Measured Conductance}) \times 100}{\text{Measured Conductance}}$$

Reanalyze if the CPD is outside the range from -40% to +10%.

Calculated Conductance = [(H⁺)(350) + (HCO₃⁻)(44.5) + (Ca²⁺)(59.5) + (Cl⁻)(76.3) + (Mg²⁺)(53.0) + (K⁺)(73.5) + (Na⁺)(50.1) + (NO₃⁻)(71.4) + (SO₄²⁻)(80.0) + (NH₄⁺)(73.5) + (OH⁻)(198) + (PO₄³⁻)(69.0)] ÷ 1000 where ionic concentrations are expressed in µeq/L.

Source: *Standard Methods for the Examination of Water and Wastewater*, 16th edition [Franson (ed.), 1985] with updated conductance factors from the 70th edition of the *CRC Handbook of Chemistry and Physics* [Weast (ed.), 1989].

2.0 Screening and Reporting Noncompliance with Data Quality Objectives

Bimonthly, the CAL QA Specialist conducts QA meetings with the CAL staff. The NADP QA Manager is invited to attend. These meetings include discussions of the results and evaluation of internal QA program analyses and of any problems within the laboratories. Use of control charts, improvement of analyses, and any proposed method changes also are discussed.

The USGS provides annual QA reports of the USGS external QA programs (interlaboratory comparison program and the NTN field blank program) to the PO.

The CAL QA Specialist prepares an annual QA report that discusses precision and bias as well as all CAL QA activities during the calendar year. Before publication, the QA report is peer reviewed and sent to the ISWS editor.

Documents required to support the QC/QA activities of the analytical laboratory consist of log books, SOPs, the CAL standards method manual (Peden et al., 1986), and this CAL QAP.

- The analyst's log book maintained by each analyst contains a record of working standards preparation, reference sample results, and daily notes. The analyst's log book may be combined with the instrument log book and the standard solution log book.
- The instrument log book is maintained at the workstation for each instrument and contains the maintenance schedule, performance record of scheduled and unscheduled maintenance, daily instrument settings and calibration data, and observations. The instrument log book may be combined with the analyst's log book and the standard solution log book.
- The standard solution log book contains all information pertinent to preparation of stock standard solutions, including all weights and volumes, confirmatory analyses, and a shelf life table. The standard solution log book may be combined with the instrument log book and the analyst's log book.
- Appendix A contains a complete list of SOPs.
- Peden et al. (1986) is an EPA document used as a reference document. When it was written, it contained complete procedures for each constituent measured, including applicable range, known interferences, calculations, a statement of precision and bias, reporting units, and significant figures reported. Methods have been modified since 1986 with the addition of new instrumentation and new computerized data acquisition systems with NOS approval.
- A copy of the CAL QAP (this document) must be kept in each laboratory.

3.0 Corrective Actions

Depending on the analytical or CAL procedure, different corrective actions must be followed. For example, shipping and receiving is handled differently than the analytical processes in the laboratory. However, each process is important and has specific corrective actions for noncompliance. It is the QA Specialist's job to determine which

processes are out of compliance and the CAL Director's responsibility to implement changes necessary to correct them.

Sample processing corrective actions are similar for both AIRMoN-wet and NTN.

If a sample is NOT assigned an alphanumeric designation and that alphanumeric designation also is NOT recorded on the FOF or the FORF, laboratory personnel receive a written notification of inadequate job performance, and a copy is sent to the CAL Director. Should this situation persist, the CAL Director takes necessary actions to correct the situation.

If errors are found during the duplicate entering of field data into the computer, the correct information is determined, and the verified data are entered into the database.

If analysis of pH and conductivity has not been done within one week of sample arrival at the laboratory (AIRMoN-wet) or within 72 hours of sample log-in (NTN), staff are alerted and notified in writing of the correct procedure. If the correct procedure still is not followed, the CAL Director implements system changes to correct the problem.

If AIRMoN-wet samples are not analyzed in sequence, especially for samples of less than 35 mL, analysts receive verbal reminders of the proper procedures. If the problem persists, the analysts receive, in writing, proper protocols for the procedures. If the problem persists, the CAL Director implements system changes to correct the problem.

When specified equipment and supplies cannot be obtained, equivalent replacements must be located by the CAL Director. The new equipment specifications must be the same or similar enough to be indiscernible from the original. For any supplies with which the samples may come into contact, a series of blanks must be obtained after cleaning to confirm that there will be no sample contamination. For other supplies, tests may need to be run to confirm that new supplies are similar to old supplies. If they are not similar, another source of supply must be found.

Standard Operating Procedures are in place for all sample chemical analysis for both AIRMoN-wet and NTN. These SOPs contain detailed information on analytical problems to avoid and suggestions for corrective actions when problems occur.

Analytical methods used by the CAL must conform to those listed in Table 4. Whenever new methods are used, there must be extensive comparisons to confirm that the two methods provide comparable results. The new method, to be accepted, must equal or exceed the old method in all aspects: bias, precision, and detection levels. It is the NADP policy to keep current with analytical techniques without sacrificing bias, precision, and detection limits. All changes in analytical techniques must be approved by the NADP NOS following written procedures for new method validation protocols.

When QC samples do not conform with the DQOs, the analysis method must be examined to determine if a change in procedure has caused this difference. If there is noncompliance with DQOs, the sample or samples in question must be reanalyzed. The QA Specialist contacts the analyst to check data for accuracy and for transcription errors.

If this is not the problem, or if the system was out of control (analytical check samples were not within specified control limits) during the analytical process, the analyst is asked to reanalyze the samples. The CAL Director is notified of the problem and ensures that corrective action has been taken.

If the standards used have not been confirmed using one of the methods in Section B of this QAP, then all analysis must stop until the standards are confirmed. Any sample analyzed before confirmation of standard concentrations is completed must be reanalyzed after confirmation is obtained.

All analytical standards older than 12 months must be discarded. If this is not done, samples analyzed after the 12-month expiration date of the standard must be reanalyzed.

Certain laboratory procedures are standard to all laboratories at the CAL. When improper bottles are used to store the standards, standards are discarded and remade, and all samples analyzed using those standards are reanalyzed. If analytical standards are not prepared in Class A glassware, standards are discarded and remade, and all samples analyzed using those standards are reanalyzed.

If the pipettors used to measure liquid standards for dilution are not checked for precision and bias before use or are more than 10 percent above or below the expected values when checked with the analytical or semi-micro balance, then the standards made with these pipettors are discarded, and all samples analyzed using these standards are reanalyzed. New pipettors are purchased and checked and/or the old pipettors are returned to the manufacturer for recalibration and cleaning.

If DI water used for making the standards is less than 18.0 Mohm-cm (ASTM Type I water), the standard is discarded and any samples measured with this sample are reanalyzed when a new standard made with ASTM Type I water becomes available.

Instrumental analysis procedures determine whether the instruments are working correctly and that standardization or calibration of the instruments is correct.

No analysis can be made if at least two reference samples are not measured after calibration or standardization. If the reference samples are not within the specified control limits for that parameter, i.e. are out of control, no analysis can be reported. If samples are analyzed, they must be reanalyzed after the system is back in control or after the reference sample value is measured to be within the control limits (3σ). Appendix B contains reference FR25, FR75, and FR25BLKS control and warning limits. These solutions are prepared annually and may vary slightly in target concentration.

Control charts are automatically generated for each Quality Control Sample (QCS) solution analyte with the LIMS. The true or expected value of each analyte for each solution is determined before the sample is used as a QCS. The warning limit for each analyte and each control solution is determined as two times the standard deviation found by 7-10 replicate analyses of the solution. The control limit is three times the standard deviation. The warning and control limits are plotted and form the basis of the control chart. The LIMS updates the control charts each time the analysts send data to the LIMS

The date of the analysis is also recorded on the control chart in the LIMS. The LIMS maintains a record of the analyst operating the instruments each day.

If any single measurement of a reference sample measured to verify correct operation is outside the control limits (3σ), all analyses of samples ceases and corrective action is taken. If the instrument can not be stopped because of programming constraints or other reasons, and analyses on that instrument must continue, the results from that run may not be reported until corrective action is taken and, when necessary, reanalysis of the samples with the system in control is complete. When instrument constraints allow, a second reference sample may be measured immediately following the out-of-control reference sample to confirm or negate the instrument was out of control. If this reference sample is also out of control, the instrument is recalibrated and all samples since the instrument was in control, i.e., when the last reference sample measured was in control, must be reanalyzed. Any instrument adjustment made to bring the QA check sample into control requires complete restandardization or calibration verification. If a new solution of the check sample results in a reading within control, no further action needs to be taken.

If, during the review of the instrument QC charts, it is determined that there is a potential bias based on seven or more consecutive measurements of a reference sample on one side of the true value concentration or three or more consecutive measurements of a reference sample between the warning and control limits, then the analyst must determine why this bias has developed. Control chart theory is based on a system that when seven or more consecutive measurements are on one side or the other of the true value, the system is out of control. Likewise, three or more consecutive results between the warning and control limits indicates the system is out of control. Although neither of these situations will result in the systems being taken off line at the CAL, they still indicate serious problems with the system and must be addressed by the analyst. The analyst, with the help of the QA Specialist and the CAL Director as needed, determines the degree of corrective action to be taken.

Some possible checks that can be made to determine why the system appears to be out of control are:

- The reference solution must be checked for contamination.
- The reference solution must be checked against a certified standard.
(**Note:** Currently the National Institute of Standards and Technology (NIST) does not make certified simulated rain standards. Other companies that make them have proven to be unreliable in their target concentrations. Analysts may use commercially available standards, but usually these need to be diluted to bring them within the concentration ranges of atmospheric deposition samples.)
- A new bottle of reference solution must be measured to see if the same concentration is measured to distinguish between a contaminated or improperly calibrated reference sample and instrument malfunction
- The instrument must be restandardized.
- New standards must be prepared or obtained for instrument standardization.

If none of the above procedures bring the instrument back into control, the instrument must be checked for mechanical, electrical, or optical problems.

If the analyst cannot determine or correct the problem with the instrument, the instrument service representative is contacted to repair or replace the instrument.

All equipment used by the CAL that comes into contact with precipitation samples or with another supply or part that comes into contact with precipitation samples is checked to ensure no contamination resulted from the contact.

If any buckets, lids, or bottles selected for random contamination checks are determined to be contaminated, the contaminated bucket, lid, or bottle is visually inspected to ascertain if the contamination is obvious as not being thoroughly cleaned. If the bucket, lid, or bottle is severely contaminated or the structural integrity of the bucket, lid, or bottle is compromised, the bucket, lid, or bottle is discarded. If there is no physical evidence of contamination, the bucket, lid, or bottle is rechecked to verify that the contamination was in the bucket, lid, or bottle not contaminated during analysis and handling of the sample. If the bucket, lid, or bottle is still contaminated, it is rewashed and rechecked. If it is still contaminated, it is discarded. If the supplies are consistently contaminated, the overall procedure for cleaning and storing the supplies is scrutinized to determine if the contamination was external or internal to the cleaning process. If there seems to be no obvious cause for contamination, additional buckets, lids, etc., are pulled and checked. If need be, the entire cleaning process is reviewed to determine if the SOPs are being followed, if the washer needs to be cleaned more frequently, if there are contaminants present in the wash room, if handling protocols are being followed, or protocol changes are needed, in an attempt to ensure clean supplies for the sites.

If the difference between the replicate samples processed randomly during analysis or reanalysis is greater than 10 percent, the replicate and/or the original sample must be reanalyzed. If the replicate still differs by more than 10 percent, the difference is noted on the reanalysis sheets and the original data must be checked to confirm that all systems were in control and that no transcription or typographical errors occurred during analysis. If no obvious error during analysis is found, the samples analyzed adjacent to the replicate may need to be remeasured to ensure that there was no contamination problem with the instrument.

If the measured concentrations of the internal blind samples exceed the 3σ control limit, this bias in the laboratory analysis must be addressed. The reference sample values must be checked for bias and precision. Calibration or standardization of the instruments must be evaluated. If the problem persists, analysis must cease until the cause for the bias or precision problem is found and corrected.

Section D of this publication reviews data verification for field data entry.

For reanalysis samples, if differences are found between the original analytical data and the randomly chosen samples for reanalysis, no data correction can be made unless it can be proven that there was an error in the original analyses. If there is an error, samples adjacent to the randomly chosen sample must be checked and reanalyzed to ensure that the problem did not exist for adjacent samples. Samples that are identified for reanalysis due to IPD or CPD must be checked carefully to ensure that if there is a real, statistical

difference in analytical results between the original sample and the reanalysis sample, that the difference is the result of an analytical error, not the result of the sample changing over time. If there is a contaminant in the sample, the degree of contamination is important in evaluating the reanalysis concentrations. Only with written justification and authorization by the QA Specialist, can an analytical value be changed.

Performance and systems audits are a routine part of the CAL operations. If the results from any interlaboratory comparison samples indicate a problem within the laboratory, those samples must be reanalyzed and the instrument and the calibration or standardization samples must be checked against a certified standard to verify that the instrument is operating properly and that the standardization or calibration is correct.

Preventative maintenance/service keeps instruments in peak operating condition. Instruments that are not maintained to perform at peak condition cannot be used for sample analysis until they are operating properly. Instruments that are taken out of service for repairs must be clearly marked and signed and dated by the QA Specialist.

Service maintenance agreements, preferably with the instrument manufacturer, are purchased when possible. All recommended servicing of the instruments is done according to the manufacturer's suggested time schedule.

For instruments without service maintenance agreements, routine calibration of the electronic components must be performed and any problems reported to the CAL QA Specialist. The CAL QA Specialist and the CAL Director, determine whether the instrument is still within manufacturer's specifications. If not, the instrument is sent in for repair and maintenance.

A pH Checker (Extech Instruments) is used to check the pH meters. To ensure that the pH meters are operating properly and are internally calibrated correctly, a self-test program on the pH meters is run at least annually or whenever there is a power failure.

For analytical instrumentation without service maintenance agreements, if routine maintenance by analysts does not correct instrument problems, the company service representative must be contacted.

D. Data Management Operations

1.0 Computer Hardware and Software

Computer hardware selection should be based on the project requirements for data storage, retrieval, and processing. Hardware purchased from approved vendors should have warranty periods consistent with industry norms. In selecting computers and peripherals, consideration also should be given to compatibility with existing hardware and software applications. The ISWS Information and Technology Committee and the Computer Services Coordinator should be consulted when selecting computer hardware.

Computer software should be purchased from an approved bidders' list or a list of authorized vendors, when possible. Software must be selected to ensure compatibility with the host hardware. Upon software receipt, the version number must be documented with the effective date that it was placed into service. If the software is to perform mathematical or computational functions, a listing of all formulas and algorithms used must be documented as well. For certain types of software, a source code listing may be required to modify or customize the software for specific applications. Computer software covered under this section includes design, data handling, data analysis, modeling, data acquisition, geographic information system scripts, and database programs.

Internally developed software, including mathematical models, must be designed with input from all planned or potential users of the program(s). The software must contain adequate documentation clearly stating the purpose and limitations of the program and applications for which the software was developed. The author of the software must be identified, and a complete program listing of the source code must be available to users. All mathematical algorithms used in the software are described in a narrative description that accompanies the source code. Prior to use, newly developed software must be rigorously tested using predetermined acceptance criteria. For mathematical models, comparison of newly developed model results with other similar model outputs is recommended. Manual calculations must be conducted on test data sets to confirm the reliability of the software prior to routine use.

Data management procedures are in place to ensure that data integrity is not compromised during data entry, electronic capture from automated instruments, or transfers between computers and databases. Written procedures to ensure the accuracy and reliability of computerized data products are described in task-specific SOPs developed for data verification purposes. Data verification methods shall include double entry of manually entered data and thorough data review procedures.

Data management and analysis for NTN and AIRMoN-wet are slightly different and are discussed separately.

2.0 NTN Description

The NTN data staff at the CAL are responsible for computerized data files and databases, data retrievals, data procedures, and data programs that summarize, check, screen, edit, and report data to participating sites and the NADP PO. Data are compiled from sample receipt observations and measurements, FORFs, analytical measurements, and other information sources (e.g., telephone communications, e-mail, and faxes) to produce a reportable record for each NTN sample (Figure 4).

Various databases are maintained to store sample descriptive and analytical information, site contact and equipment information, and edit logs. The RBASE relational database and the SQL server relational database are the two primary databases used for these purposes.

When the precipitation sample and FORF are received at the CAL, the white copy is separated from the yellow copy, and the raingage chart is stapled to the yellow copy. All information on the FORF is typed into the LIMS.

A series of “rules” incorporated in the computerized data entry form restrict data entries to an acceptable set of dates, integers, character strings, or range of real numbers (see SOP DATA-01 for details on these rules).

Sample receiving personnel sort the yellow copies and raingage charts for various screening protocols and then forward these to the Site Liaison. White copies of FORFs are sent in batches of 100 for double entry in a duplicate database (for details about these procedures, see SOPs DATA-01, and DATA-10).

During FORF sorting and screening, sample receiving personnel identify certain problems that require faxing the sites for clarification. This procedure has helped to facilitate faster resolution of FORF errors or incomplete information (see SOP DATA-01 for additional details).

FORF data and chemical analysis results are loaded from the LIMS into the RBASE database KEDNEW. Samples are loaded in predetermined blocks. Block size varies depending on the number of samples received each month from NTN sites and has included up to 1200 samples. This number can change as the number of sites increases or decreases.

The NTN Database Manager compares double-entered FORF values and reconciles any differences. This is completed by checking the disparate entries against the original FORF and ensuring data in the original file are correct.

A series of checks are run from the LIMS which flag samples having unusual collector or raingage function or precipitation data. The data technician responsible for the initial data

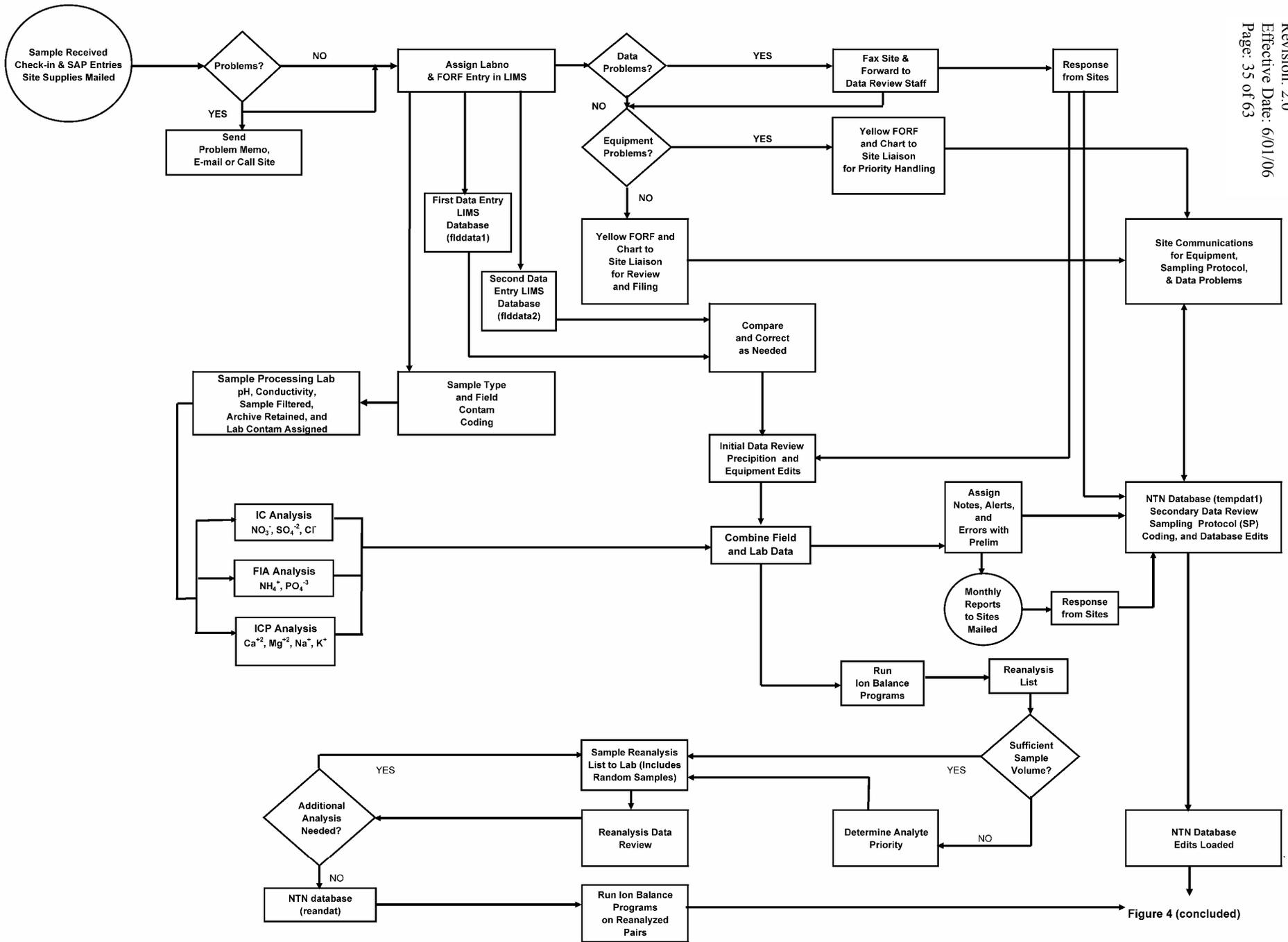


Figure 4. Sample Processing and Data Flowchart, NTN

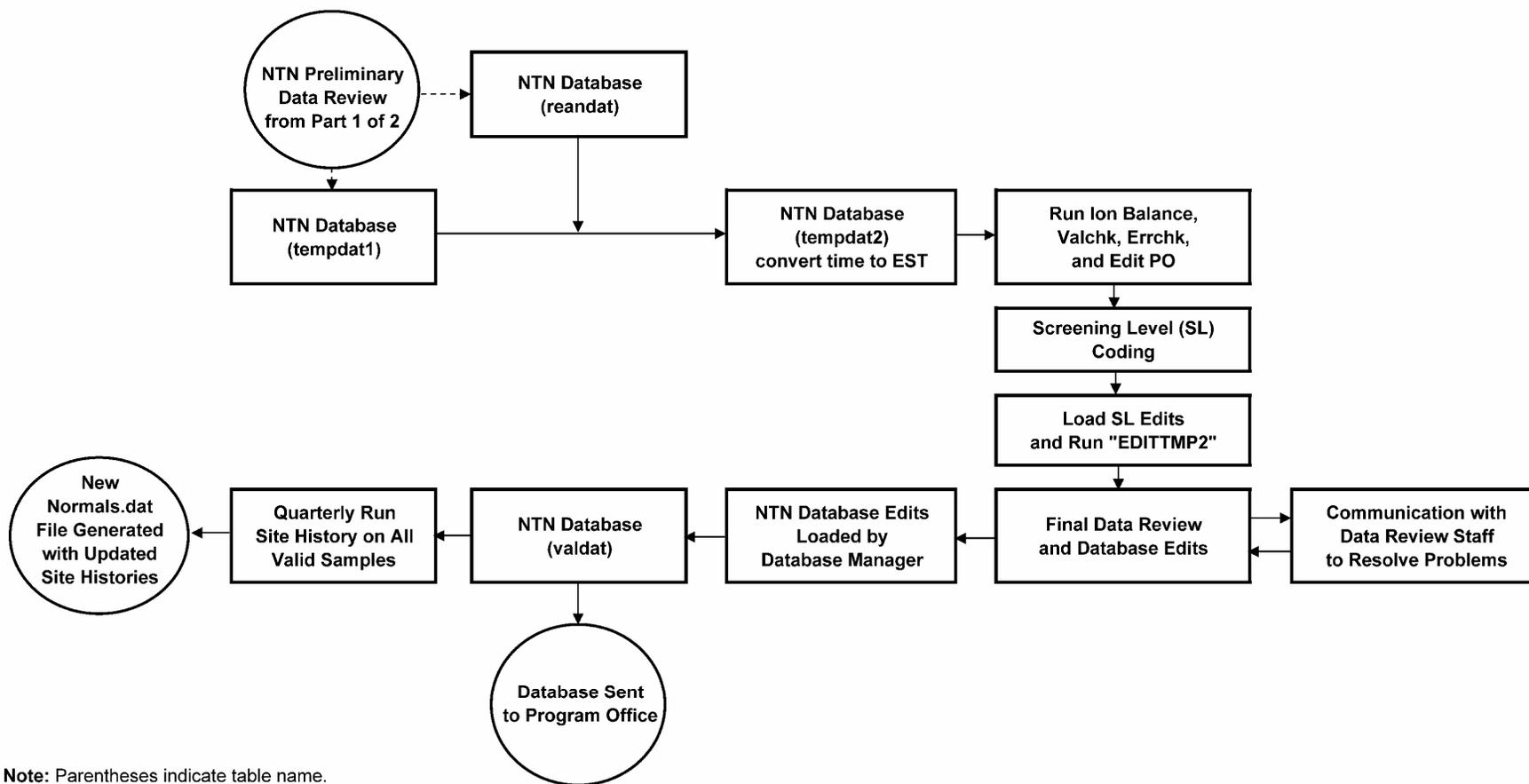


Figure 4 (concluded)

review checks the FORF and raingage chart for each flagged sample. Edits are based on site communication and re-readings of the raingage chart and FORF.

The NTN Database Manager uses appropriate programs to edit the KEDNEW database and load edits into an edit log database. These programs require a match between what is in the database and station ID, lab identification number, and current value of a field to be edited. When these fields match, the current value in the database can be edited to a correct new value (see SOP DATA-10). Tables containing field and laboratory data are then loaded from the KEDNEW database and merged in the NTN database table TEMPDAT1.

The “IONBAL” program is run on this set of samples. Various checks in this program ensure sample validity. One such check confirms the completion of each record (see SOP DATA-01 for a complete set of checks).

Each month the CAL issues site-specific printouts to each NTN site operator and supervisor. These printouts include preliminary results of chemical analyses and FORF information provided by the sites with notes, alerts, and error messages generated by computer programs at the CAL to provide feedback and encourage correction and verification of unusual data. Information facilitating ongoing communication between the sites and the CAL is included with each printout (see SOP DATA-10). The CAL Administrative Assistant mails the printouts to the sites. Exact procedures may be found in the Administrative Assistant Training Manual.

The NTN Site Liaison is responsible for secondary review of NTN data to verify accuracy in all field data and preliminary edits and to apply sampling protocol validation codes for each sample. A series of checks, including those utilized in preliminary review and for all other field data (e.g. gaps between samples or sample duration overlaps), are generated by the NTN Database Manager. Edits to the data set are based on faxes, phone calls, notes from sites, raingage charts, and FORFs. The NTN Site Liaison also verifies daily precipitation amounts and reconciles those data with daily precipitation types and sampling duration (see SOP DATA-15 for complete details).

On or about the tenth day of each month, the NTN Site Liaison gives the NTN Database Manager a set of edits to be made to TEMPDAT1 in the NTN database. After edits have been applied and archived in the NTNLOG database, the data set is moved between tables to TEMPDAT2 in the NTN database. The NTN Database Manager then takes custody of the data to conduct the final screening of the data prior to releasing the data set to the PO.

The primary goal in the final review is to satisfy final CAL checks of data custody, verification, and screening, and to document data quality and representativeness. Various programs run by the NTN Database Manager facilitate this final review process (see SOP DATA-10).

The “SCRNSL” program automatically identifies samples that receive a Screening Level (SL) code. These codes identify samples compromised through mishandling, storage,

measurement, or contamination (see SOP DATA-19 for details about this coding).

The "IONBAL" program is run on reanalysis pairs. The reanalysis ion balance printout displays the original analysis and reanalysis for each sample side by side for comparison. An asterisk denotes differences greater than 10 percent between the original and reanalysis values for any analyte. Once identified, a reason for the difference is determined for each sample. Is the sample chemistry changing? Was there an error in the original analysis? Was there an error in reporting the original values? Depending on the answers to these questions, the CAL Database Manager recommends changing the original values to the reanalysis values or leaving the original values in the database. For more details concerning the evaluation of the reanalyzed samples, see SOP DATA-19.

On or about the 20th day of each month, the NTN Database Manager applies edits to the database as a result of the data screening. Appropriate programs are used to edit the database and load edits into an edit log database (see SOP DATA-10).

After the edits are made, the NTN Database Manager copies the latest version of the databases to the PO file space and informs the PO that the new databases are available. A memo is sent to the PO indicating the sample sequence and documenting new sites, discontinued sites, site moves or significant changes, site reopenings, missing samples, sample gaps greater than three hours, and late samples. The white copies of the relevant FORFs accompany the memo.

The CAL maintains a site information database used to store, report, and update data pertaining to each site's history. This database facilitates CAL/site communications and contains entries for personnel, field equipment, laboratory equipment, site location, and site status (see SOP DATA-11 for a detailed description of stored data and the uses of this information).

Archived site information files maintained at the CAL for each active and inactive network site include notes pertaining to sampling gaps, site moves, siting variances, and subsampling requests.

The NTN Site Liaison has specific duties and responsibilities beyond the secondary NTN data review.

- The NTN Site Liaison provides communications between sites and the CAL via e-mail, telephone calls, and faxes.
- The NTN Site Liaison confers with individual sites about equipment use and malfunctions, questions and errors for review purposes, siting regulations, and general network operations.

- The use of Microsoft Outlook Journal facilitates communications within the CAL to record phone conversations and convey information to the NTN Data Technician and NTN Database Manager during the data review process.
- Prior to the secondary data review the NTN Site Liaison reviews each FORF for mention of equipment and collection problems (see the SOP DATA-13 for further details).
- The NTN Site Liaison assigns sampling protocol codes after reviewing the FORFs. Sampling protocol describes the conditions under which an NTN sample is collected. Sample collection buckets should be uncovered and exposed to the atmosphere only during precipitation and remain covered at all other times. This is defined as wet-only sampling. The NTN samples are considered wet-only samples when the exposure to dry weather is six hours or less. These samples are assigned a blank sampling protocol code. Samples open or exposed continuously throughout the sampling period are assigned a sampling protocol code of “B” (bulk samples). Quality assurance samples are assigned a sampling protocol code of “Q”. All other samples are assigned a sampling protocol code of “U” (undefined samples).
- E-mails from sites pertaining to data corrections are forwarded to appropriate data management staff.

The NTN Database Manager completes a quarterly review of data from which archives are created. This record includes:

- Transmittal memos to the PO.
- List of samples to be remeasured due to ion percent differences (wet samples only).
- List of samples to be remeasured due to conductance percent differences (wet samples only).
- Reanalysis ion balance printouts.
- “VALCHK” printouts that contain outlier chemistry data for each sample (see SOP DATA-19 for details).

The “ERRCHKAR” and “IONBALANCE” printouts are maintained only until the data are transferred to the Program Office. The “REANALYSIS” and “VALCHK” printouts are maintained permanently.

The CAL policy for record archives for data management is similar to the record archives policy for the laboratory.

FORF and raingage chart retention:

- White copy (FORF): after final validation by the CAL and transmittal to the PO, white copies are kept for two years in the PO Database Manager’s office before being discarded.
- Yellow copy (FORF): after final data are transmitted to the PO, the yellow copies are discarded.

- Raingage charts: Charts are detached from the yellow copy of the FORF and are kept permanently. The lab number, site ID, and date off are written on the chart. The PO files the charts by site and date off.

All manually recorded lab sheets generated prior to laboratory instrument automation are kept permanently.

All correspondence with sites pertaining to data updates or corrections is retained for two years after transmittal of final data to the PO and then discarded. Correspondence with sites concerning sampling gaps, site moves, siting variances, and subsampling is kept permanently.

Most site files are maintained permanently, including Site Visitation/Audit reports, U.S. Geological Survey (USGS) contour maps and other miscellaneous maps, Site Description Questionnaires, Site Location information (memos and pamphlets), correspondence concerning site start-ups and visitations, and pictures and slides updated as site visitations are conducted.

3.0 AIRMoN-wet Description

Data management staff at the CAL is responsible for AIRMoN-wet computerized data files and databases, data retrievals, and procedures and programs that summarize, check, screen, edit, and report data to participating sites and to the NADP PO. Data are compiled from site operator observations, CAL observations upon sample receipt, FOFs, analytical measurements, and other information sources (e.g., telephone communications, e-mail, and faxes) to produce a reportable record for each AIRMoN-wet sample. See Figure 5 for the AIRMoN-wet sample processing and data flowchart.

Various databases maintained by data management staff store sample descriptions, analyses, and other information (site contacts, equipment, and edit logs). The RBASE relational database is the primary database used for these purposes.

The CAL receives the precipitation sample, raingage chart, and FOF with the sample and temperature bottle surrounded by Ice Brix®. The CAL receiving room personnel open the black mailer box, measure the temperature of the “temperature only” bottle, and record this information on the FOF (see SOP PREP-54 for complete details).

The information on the white copy (FOF and Laboratory Observer Form or LOF) is entered into an RBASE database. The same information is reentered into a duplicate database and compared for accuracy (see SOP DATA-56 for complete details).

After the double entry is complete, the two databases are compared and the AIRMoN-wet Database Manager reconciles the differences by checking the disparate entries against FOF and LOF data and ensuring the data in the original file match FOF and LOF data.

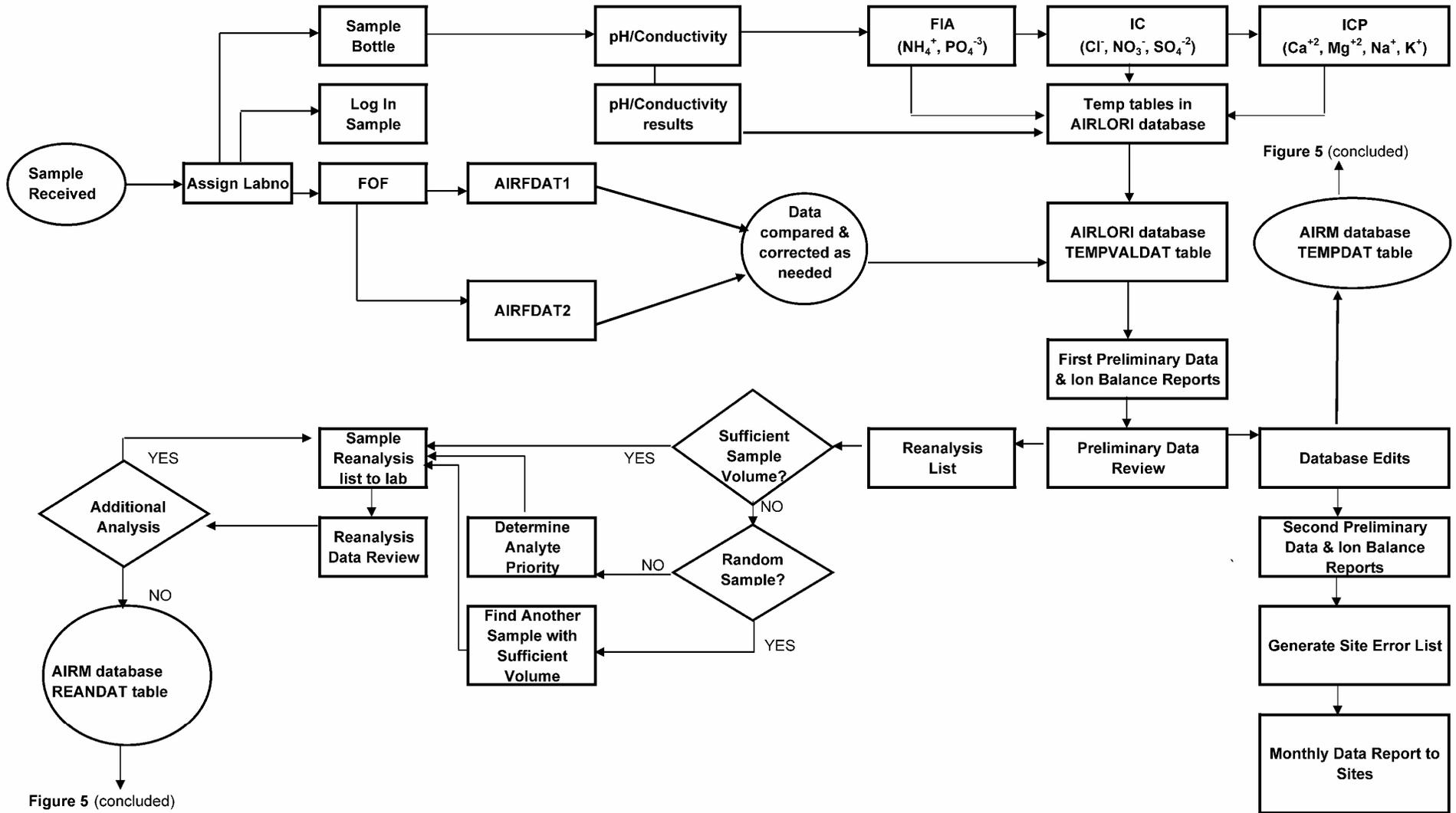


Figure 5 (concluded)

Figure 5. Sample Processing Data Flow Chart, AIRMoN-wet

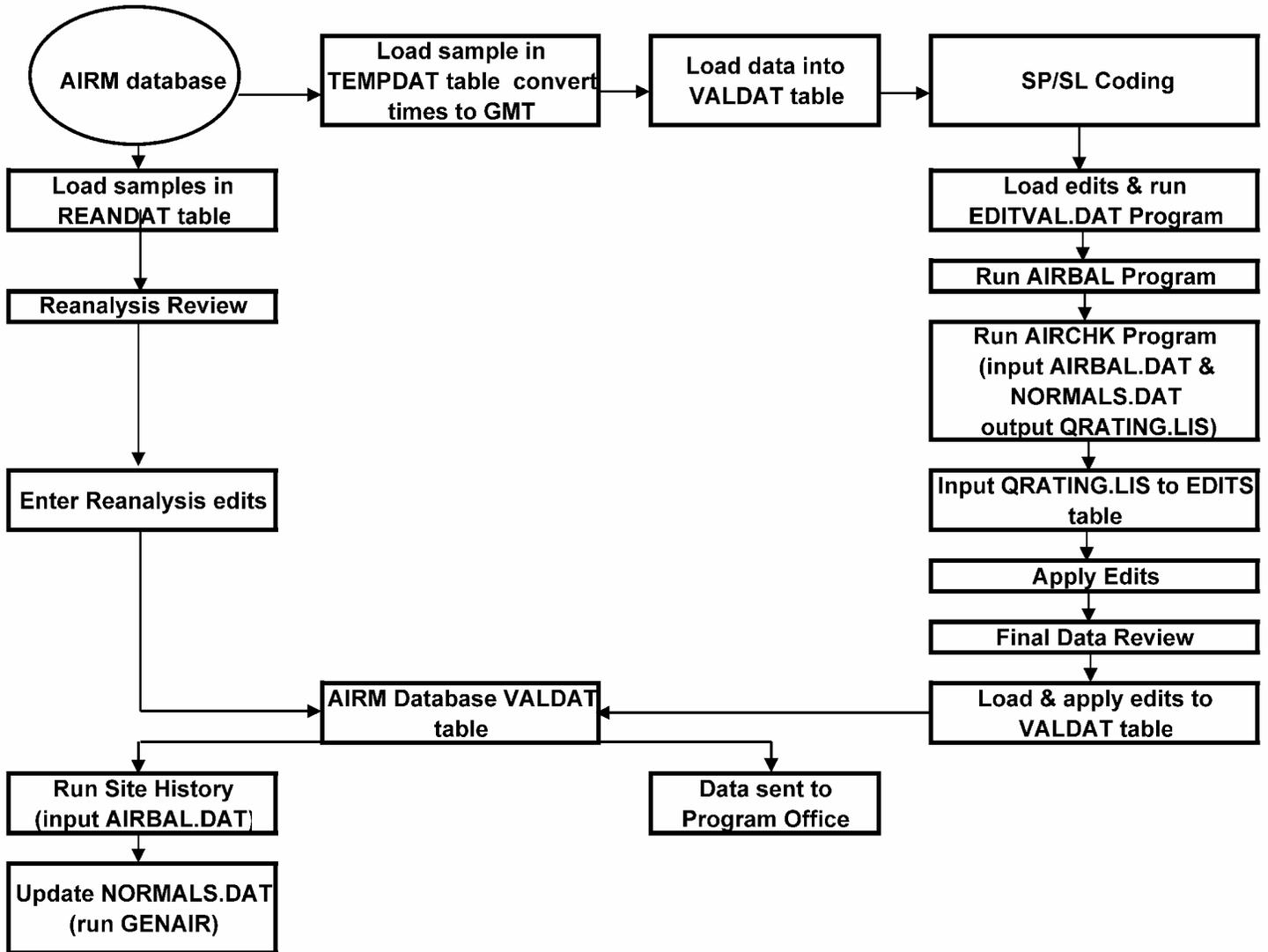


Figure 5 (concluded)

The AIRMoN-wet Liaison reviews each FOF and recommends changes. The AIRMoN-wet preliminary data review and reporting uses some of the same programs as NTN data review and reporting but modified for the AIRMoN-wet daily sampling protocols (see SOP DATA-58 for complete details).

After all the FOF information has been entered into the database, the AIRMoN-wet Database Manager combines this information with laboratory data received from the CAL AIRMoN-wet analysts. Laboratory analyses go directly into the LIMS and are retrieved from there electronically and loaded into RBase by the AIRMoN-wet Database Manager where they are merged with the field data.

Between the first and the fifth day of each month, the AIRMoN-wet Database Manager generates preliminary printouts of analytical and field data printouts of the analytical data for the previous month for the AIRMoN-wet Liaison to review. Preliminary printouts are organized by site and contain the sample type, date and time on and off, field chemistry, laboratory chemical concentrations, and the deposition of the analytes in milligrams/square meter. The ion balance and the IPD and CPD are generated from the LIMS and are used to determine samples which need reanalysis. Samples identified in this manner as well as 2% of randomly selected monthly samples are sent to the laboratory for reanalysis.

After reviewing preliminary data printouts, the AIRMoN-wet Liaison submits necessary data edits to the AIRMoN-wet Database Manager. Revised preliminary printouts and electronic copies are generated for the AIRMoN-wet Liaison.

The AIRMoN-wet Liaison e-mails a monthly printout for review along with a summary e-mail to the site operator and the primary sponsor of the AIRMoN sites. These e-mails include the computer generated problems as well as the preliminary data and other information needed by the site operators to review the preliminary data.

After site personnel receive and review the monthly preliminary data reports, they send any updates or corrections to the AIRMoN-wet Liaison, who generates an edit file in RBASE. This file is sent to the AIRMoN-wet Database Manager. The laboratory identification number, the station ID, and the current data value for the edits must match the ones in the database in order for the edits to be affected.

Between the fifth and the tenth of each month, the sample set is transferred to the final database, and sample on and off times are converted to Greenwich Mean Time.

Chemistry reanalyses from the previous month are entered directly into an AIRMoN reanalysis table in the LIMS. The AIRMoN-wet Database Manager transfers this data into the appropriate table in RBase when notified that the reanalysis results have been entered.

The reanalysis sample ion balance generated with the LIMS is reviewed along with the original sample data and ion balance results. Any edits are included in the final review edits and sent to the AIRMoN-wet Database Manager.

The AIRMoN-wet Database Manager runs the “SITE HISTORY” program to compute a tolerance level for uncontaminated samples for each site (i.e., what is considered “normal” for that site). It includes values from the 5th to the 99th percentile levels for all analytes. These historical ranges are used to determine whether other samples from that site are contaminated. Concentrations are site dependent (see SOP DATA-58 for complete details).

The AIRMoN-wet Database Manager runs the “AIRCHECK” program to determine whether analyte concentrations for a sample with visible contaminants are within normal ranges expected for that site. If the concentrations of the analytes are outside the normal range, based on the history of that site, the sample is considered contaminated and coded as such (see SOP DATA-58 for complete details).

The AIRMoN-wet Database Manager makes data changes generated by the “AIRCHECK” program, including Sampling Protocol, Screening Level, and Quality Rating codes, and those generated by the AIRMoN-wet Liaison’s final review of the FOFs (see SOP DATA-58 for complete details).

The AIRMoN-wet final data review and reporting is similar to that for NTN. Between the tenth and 21st day of each month, a final data review is conducted of the FOFs, reanalysis values, and raingage charts. Edits generated from this final review are implemented, and the data are sent to the PO for inclusion in the PO database, accessible on-line through the Internet.

Sample retention policy for AIRMoN-wet differs from that for NTN in that no AIRMoN-wet samples are permanently archived. The AIRMoN-wet samples must be archived for two years after data have been published.

The AIRMoN-wet Liaison maintains all “AIRCHECK”, “PRELIMINARY DATA”, “SITE HISTORY”, “REANALYSIS”, and edit log printouts (see SOP DATA-58 for complete details) for the duration of the project.

The AIRMoN-wet Liaison keeps copies of preliminary data letters sent to the sites. For the duration of the project, all electronically submitted preliminary data letters are maintained on the AIRMoN-wet Liaison’s computer, which is backed up weekly.

For the duration of the project, the AIRMoN-wet Liaison keeps all communications from the Site Operators to the CAL as paper copies or on the computer.

E. Terms and Definitions

audit (quality) - a systematic and independent examination to determine whether quality activities and related results comply with planned arrangements, and whether these arrangements are implemented effectively and are suitable to achieve objectives.

bias - a persistent positive or negative deviation of the measured value from the true value. In practice, bias is expressed as the difference between the value obtained from analysis of a homogeneous sample and the accepted true value.

data quality assessment - a statistical and scientific evaluation of the data set to determine the validity and performance of the data collection design and statistical test, and to determine the adequacy of the data set for its intended use.

data quality objectives (DQOs) - the qualitative and quantitative measures of data quality desired from a specific activity or program. DQOs may include characteristics of bias, precision, completeness, and representativeness.

environmental data - any measurements or information describing environmental processes, location, or conditions; ecological or health effects and consequences; or the performance of environmental technology. Environmental data include information collected directly from measurements, produced from models, and compiled from other sources such as databases or the literature.

independent assessment - an assessment performed by a qualified individual, group, or organization separate from the organization directly performing and accountable for the work being assessed.

management - those individuals directly responsible and accountable for planning, implementing, and assessing work.

management system - a structured, nontechnical system describing the policies, objectives, principles, organizational authority, responsibilities, accountability, and implementation plan of an organization for conducting work and producing items and services.

management systems review - the qualitative assessment of a data collection operation and/or organization(s) to establish whether the prevailing quality management structure, policies, practices, and procedures are adequate for ensuring that the appropriate type and quality of data are obtained.

peer review - an in-depth assessment of the assumptions, calculations, extrapolations, alternate interpretations, methodology, acceptance criteria, and conclusions pertaining to specific work and of the supporting documentation by qualified individuals or an organization independent of those who performed the work.

performance evaluation - a type of audit in which the quantitative data generated in a measurement system are obtained independently and compared with routinely obtained data to evaluate the proficiency of an analyst or laboratory.

quality assurance (QA) - an integrated system of management activities involving planning, implementation, documentation, assessment, reporting, and quality improvement to ensure that a process, item, or service is of the type and quality needed and expected by the client.

quality assurance project plan (QAPP) - a formal document describing in comprehensive detail the necessary QA, QC, and other technical activities that must be implemented to ensure that the results of the work performed will satisfy stated performance criteria.

quality control (QC) - the overall system of technical activities that measures the attributes and performance of a process, item, or service against defined standards to verify that they meet the stated requirements established by the customer; operational techniques and activities that are used to fulfill requirements for quality.

quality improvement - a management program to improve the quality of operations. A management program generally entails a formal mechanism for encouraging worker recommendations with timely management evaluation and feedback or implementation.

quality management - that aspect of the overall management system of the organization that determines and implements the quality policy. Quality management includes strategic planning, allocation of resources, and other systematic activities (e.g., planning, implementation, documentation, and assessment) pertaining to the quality system.

quality management plan (QMP) - a document describing the quality system in terms of organizational structure, functional responsibilities of management and staff, lines of authority, and required interfaces for those planning, implementing, and assessing all activities conducted.

record - a completed document providing objective evidence of an item or process. Records may include photographs, drawings, magnetic tape, and other data recording media.

specifications - a document that states requirements and which refers to or includes drawings or other relevant documents. Specifications should indicate the means and the criteria for determining conformance.

standard operating procedure (SOP) - a written document detailing the method for an operation, analysis, or action with thoroughly prescribed techniques and steps; the officially approved method for performing certain routine or repetitive tasks.

supplier - any individual or organization furnishing items or services or performing work according to a procurement document or financial assistance agreement. This is an all-inclusive term used in place of any of the following: vendor, seller, contractor, subcontractor, fabricator, or consultant.

technical review - an in-depth analysis and evaluation of documents, activities, material, data, or items requiring technical verification or validation for applicability, correctness, adequacy, completeness, and assurance that established requirements are satisfied.

technical systems audit - a thorough, systematic, on-site, qualitative audit of facilities, equipment, personnel, training, procedures, record keeping, data validation, data management, and reporting aspects of a system.

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Appendix A

List of CAL Standard Operating Procedures (SOPs)

CAL Standard Operating Procedures (SOPs)

<i>SOP #*</i>	<i>Title</i>
COND 01	The Determination of Conductivity
DATA-01	Field Observer Report Form (FORF)
DATA-10	Management of the NTN CAL Databases
DATA-11	Maintenance of the CAL Site Information Database
DATA-12	Evaluating NTN Sample Gaps and Lags
DATA-13	Review of NTN Wet Bucket Data
DATA-14	NTN Equipment and Precipitation Data Review
DATA-15	Review of the NADP/NTN Data
DATA-16	Reanalysis Procedures for NTN and AIRMoN
DATA-19	Final Review of NADP/NTN Data
DATA-31	Computer Backup and Recovery
DATA-35	Computer Hardware and Programs, Procedures, and Software Used by the NADP/NTN/CAL Data Management Group
DATA 36	NADP Proprietary Software General Notes and Information
DATA-40	Sample Coding for Non-AIRMoN and Non-NTN Precipitation Samples
DATA-51	Field Observer Form (FOF) Data Entry for the AIRMoN
DATA-53	Reanalysis Data Entry for the AIRMoN
DATA-56	AIRMoN Preliminary Database Management and Creation of Preliminary Reports
DATA-57	AIRMoN Final Database Management

***Note:** The alphanumeric number preceding the decimal is a unique number for each SOP and is organized by SOP type.

CAL Standard Operating Procedures (SOPs) (continued)

<i>SOP #*</i>	<i>Title</i>
DATA-58	AIRMoN Preliminary Data Review
DATA-59	AIRMoN Monthly Final Data Review
FIA-01	The Determination of Ammonium (phenolate) by Flow Injection Analysis
FIA-02	The Determination of Orthophosphate by Flow Injection Analysis
FIA-03	The Determination of Total Nitrogen
IC-01	The Determination of Cl^- , NO_3^- , and SO_4^{2-} Using Dionex DX-500 Ion Chromatographs
IC-02	The Determination of Cl^- , NO_3^- , and SO_4^{2-} Using Dionex ICS-2000 Ion Chromatographs
ICP-01	The Determination of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ by Inductively Coupled Plasma-Optical Emission Spectroscopy
PH-01	The Determination of pH
PREP-02	Sample Filtration for the NTN
PREP-03	Bucket and Bottle Preparation
PREP-05	Electrode Evaluation and Shipment
PREP-06	4.3 Quality Control Check Sample Preparation
PREP-07	Specific Conductance Standard Preparation
PREP-08	4.9 Quality Control Check Sample Preparation
PREP-09	Sample Inspection and Contamination Coding
PREP-10	USGS Interlaboratory Comparison Studies
PREP-11	Preparation of Weekly Blanks

***Note:** The alphanumeric number preceding the decimal is a unique number for each SOP and is organized by SOP type.

CAL Standard Operating Procedures (SOPs) (concluded)

<i>SOP #*</i>	<i>Title</i>
PREP-12	Preparation of Simulated Rain Samples
PREP-13	Reverse Osmosis Maintenance
PREP-14	Preparation of High Concentration Check Sample for ICP
PREP-15	Shipping and Receiving of NTN Site Supplies
PREP-16	Sample Receiving for NTN
PREP-54	Sample Shipping and Receiving for AIRMoN
QA-01	Quality Assurance Report
QA-02	WMO/GAW Interlaboratory Comparison Sample Preparation
QAP-01	Quality Assurance Plan

***Note:** The alphanumeric number preceding the decimal is a unique number for each SOP and is organized by SOP type.

Appendix B

Control and Warning Limits for Internally Prepared QC Solutions

Table B-1. FR25 Concentrations (mg/L), 2006

<i>Parameter</i>	<i>Control (-)</i>	<i>Warning (-)</i>	<i>Mean</i>	<i>Warning (+)</i>	<i>Control (+)</i>
Ca ²⁺	0.0501	0.0509	0.0525	0.0541	0.0549
Mg ²⁺	0.0086	0.0090	0.0098	0.0106	0.0110
Na ⁺	0.0172	0.0178	0.0190	0.0202	0.0208
K ⁺	0.0057	0.0067	0.0087	0.0107	0.0117
NH ₄ ⁺	0.086	0.088	0.092	0.096	0.098
PO ₄ ³⁻ nutrient low	0.032	0.034	0.038	0.042	0.044
Cl ⁻	0.044	0.046	0.050	0.054	0.056
NO ₃ ⁻	0.559	0.566	0.580	0.594	0.601
SO ₄ ²⁻	0.493	0.501	0.517	0.533	0.541
pH (pH units)	4.90	4.91	4.93	4.95	4.96
Specific Conductance (μS/cm)	6.8	6.9	7.0	7.1	7.2

Table B-2. FR75 Concentrations (mg/L), 2006

<i>Parameter</i>	<i>Control (-)</i>	<i>Warning (-)</i>	<i>Mean</i>	<i>Warning (+)</i>	<i>Control (+)</i>
Ca ²⁺	0.254	0.257	0.263	0.269	0.272
Mg ²⁺	0.0412	0.0426	0.0454	0.0482	0.0496
Na ⁺	0.126	0.130	0.138	0.146	0.150
K ⁺	0.0336	0.0347	0.0369	0.0391	0.0402
NH ₄ ⁺	0.453	0.458	0.468	0.478	0.483
PO ₄ ³⁻ nutrient high	0.145	0.150	0.160	0.170	0.175
Cl ⁻	0.235	0.239	0.247	0.255	0.259
NO ₃ ⁻	1.875	1.890	1.920	1.950	1.965
SO ₄ ²⁻	1.872	1.887	1.917	1.947	1.962
pH (pH units)	4.57	4.58	4.60	4.62	4.63
Specific Conductance (μS/cm)	17.9	18.2	18.9	19.6	20.0

Table B-3. FR25 Blanks Concentrations (mg/L), 2006

<i>Parameter</i>	<i>Control (-)</i>	<i>Warning (-)</i>	<i>Mean</i>	<i>Warning (+)</i>	<i>Control (+)</i>
Ca ²⁺	0.0516	0.0522	0.0534	0.0546	0.0552
Mg ²⁺	0.0087	0.0091	0.0099	0.0107	0.0111
Na ⁺	0.0175	0.0180	0.0190	0.0200	0.0205
K ⁺	0.0069	0.0074	0.0084	0.0094	0.0099
NH ₄ ⁺	0.087	0.089	0.093	0.097	0.099
Cl ⁻	0.047	0.049	0.053	0.057	0.059
NO ₃ ⁻	0.566	0.574	0.590	0.606	0.614
SO ₄ ²⁻	0.495	0.505	0.525	0.545	0.555
pH (pH units)	4.89	4.90	4.92	4.94	4.95
Specific Conductance (μS/cm)	6.8	6.9	7.1	7.3	7.4

Table B-4. FR10 Concentrations (mg/L), 2006

<i>Parameter</i>	<i>Control (-)</i>	<i>Warning (-)</i>	<i>Mean</i>	<i>Warning (+)</i>	<i>Control (+)</i>
Ca ²⁺	0.0247	0.0250	0.0256	0.0262	0.0265
Mg ²⁺	0.0041	0.0044	0.0050	0.0056	0.0059
Na ⁺	0.0081	0.0084	0.0090	0.0096	0.0099
K ⁺	0.0023	0.0027	0.0035	0.0043	0.0047
NH ₄ ⁺	0.025	0.027	0.031	0.035	0.037
Cl ⁻	0.027	0.028	0.030	0.032	0.033
NO ₃ ⁻	0.269	0.274	0.284	0.294	0.299
SO ₄ ²⁻	0.206	0.213	0.227	0.241	0.248
pH (pH units)	5.06	5.09	5.15	5.21	5.24
Specific Conductance (μS/cm)	3.6	3.7	3.9	4.1	4.2

Table B-5. FR95 Concentrations (mg/L), 2006

<i>Parameter</i>	<i>Control (-)</i>	<i>Warning (-)</i>	<i>Mean</i>	<i>Warning (+)</i>	<i>Control (+)</i>
Ca ²⁺	0.706	0.720	0.748	0.776	0.790
Mg ²⁺	0.131	0.135	0.143	0.151	0.155
Na ⁺	0.661	0.670	0.688	0.706	0.715
K ⁺	0.100	0.102	0.106	0.110	0.112
NH ₄ ⁺	1.031	1.040	1.058	1.076	1.085
Cl ⁻	1.210	1.218	1.234	1.250	1.258
NO ₃ ⁻	3.722	3.754	3.818	3.882	3.914
SO ₄ ²⁻	3.853	3.882	3.940	3.998	4.027
pH (pH units)	4.46	4.47	4.49	4.51	4.52
Specific Conductance (μS/cm)	33.5	33.9	34.7	35.5	35.9

