QUALITY ASSURANCE PLAN
CENTRAL ANALYTICAL LABORATORY, 2002

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM
A Cooperative Research Support Program of the
State Agricultural Experiment Stations (NRSP-3)
Federal and State Agencies
and Private Research Organizations
In 2001, scientists, students, educators, and others interested in National Atmospheric Deposition Program (NADP) data logged nearly 110,000 sessions on the NADP Internet site. They made more than 18,000 on-line data retrievals and viewed maps nearly 88,000 times. 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 the leadership of State Agricultural Experiment Stations (SAES) 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 acidic chemicals, nutrients, and base cations. The NADP was initially 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, SAES reclassified IR-7 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, NAPAP agreed to coordinate operation of NAPAP’s National Trends Network (NTN). To benefit from shared siting criteria, identical operating procedures, and a shared analytical laboratory, NAPAP and NTN merged with the designation NADP/NTN. Many sampling sites are supported by the U.S. Geological Survey (USGS), 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 nearly 250 sites in the network, and the network designation has been shortened to NTN.

In the 1990s, NADP expanded to include two additional networks. The Atmospheric Integrated Research Monitoring Network (AIRMoN), which currently has ten sites, joined NADP in October 1992. AIRMoN sites collect samples daily when precipitation occurs. Samples are refrigerated until analysis at the CAL for the same constituents measured in NTN samples. AIRMoN seeks to identify pollutant source/receptor relationships and the effect of emissions changes on precipitation chemistry, combining measurements with atmospheric models. AIRMoN also evaluates new sample collection and preservation methods. Another NADP network, the Mercury Deposition Network (MDN), currently has nearly 70 sites and joined NADP in 1996. MDN sites collect wet-only deposition samples that are sent to a laboratory specializing in mercury measurements. Frontier Geosciences, Inc. analyzes all samples for total mercury and some samples for methyl mercury. The MDN collects data on the wet deposition of mercury to surface waters, forested watersheds, and other receptors. Forty-three 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 importance of the atmospheric deposition of mercury as a cause of this problem.

A number of federal agencies support the NADP: U.S. Geological Survey; National Park Service; Environmental Protection Agency; National Oceanic and Atmospheric Administration; U.S. Department of Agriculture - Forest Service; Bureau of Land Management; U.S. Fish & Wildlife Service; Tennessee Valley Authority; and U.S. Department of Agriculture - Cooperative State Research, Education, and Extension Service under Agreement No. 98-COOP-1-5925. Additional support is provided by various other federal agencies, State Agricultural Experiment Stations, state agencies, universities, and public and private research organizations. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the author and do not necessarily reflect the view of the U.S. Department of Agriculture or any other sponsor.

For further information, contact:
NADP Program Office
Illinois State Water Survey
2204 Griffith Drive
Champaign, IL 61820

NADP Home Page: http://nadp.sws.uiuc.edu
E-mail: nadp@sws.uiuc.edu

The Illinois State Water Survey is an Affiliated Agency of the University of Illinois and a Division of the Illinois Department of Natural Resources.
Quality Assurance Plan

Version 1.3, August 21, 2002

National Atmospheric Deposition Program
Central Analytical Laboratory
Illinois State Water Survey
2204 Griffith Drive
Champaign, IL 61820-7495

Authors: Jane Rothert
Karen Harlin
Kathy Douglas
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Approval Date: August 21, 2002
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.

Signature  M. E. Peden
Mark E. Peden,
Director of External Relations and Quality Assurance

Date  8/21/2002

Signature  Christopher M. S. Lehmann
Christopher Lehmann, Quality Assurance Manager,
National Atmospheric Deposition Network

Date  8/21/2002

Signature  Karen Harlin
Karen Harlin, Director, NADP Central Analytical Laboratory and NADP Assistant Coordinator

Date  8/21/02

Signature  Kathy Douglas
Kathy Douglas, NTN Database Manager
NADP Central Analytical Laboratory

Date  8/21/02

Signature  Jane Rother
Jane Rother, QA Specialist, NADP Central Analytical Laboratory

Date  8/21/02
Quality Assurance Plan Distribution List

Derek Winstanley, Chief

Mark E. Peden, Director of External Relations and Quality Assurance

Van C. Bowersox, Coordinator, National Atmospheric Deposition Program

Jane Rothert, NADP Quality Assurance Specialist (master copy and archive copies)

Karen Harlin, CAL Director and Assistant Coordinator, National Atmospheric Deposition Program

Kathy Douglas, Database Manager

Office Copy, CAL (Pam Bedient, Administrative Assistant)

Christopher Lehmann, NADP Quality Assurance Manager

Illinois State Water Survey Library

NADP Officers/Technical Committee members

NADP Scientific/Supervisory CAL Staff
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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\textsuperscript{th} percentile concentrations of the NADP/NTN
FR75  A synthetic rainwater solution formulated to approximate the 75\textsuperscript{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)

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<tr>
<th>Acronym</th>
<th>Description</th>
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<tr>
<td>NRSP-3</td>
<td>National Research Support Project</td>
</tr>
<tr>
<td>NTN</td>
<td>National Trends Network</td>
</tr>
<tr>
<td>PO</td>
<td>Program Office</td>
</tr>
<tr>
<td>QA</td>
<td>Quality Assurance</td>
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<tr>
<td>QA/R-5</td>
<td>EPA Requirements for QA Project Plans</td>
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<tr>
<td>QAP</td>
<td>Quality Assurance Plan</td>
</tr>
<tr>
<td>QC</td>
<td>Quality Control</td>
</tr>
<tr>
<td>QCS</td>
<td>Quality Control Standard</td>
</tr>
<tr>
<td>QMP</td>
<td>Quality Management Plan</td>
</tr>
<tr>
<td>Site ID</td>
<td>Station identification code</td>
</tr>
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<td>SL</td>
<td>Screening Level</td>
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<tr>
<td>SOP</td>
<td>Standard Operating Procedure</td>
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<tr>
<td>USEPA</td>
<td>U.S. Environmental Protection Agency</td>
</tr>
<tr>
<td>USGS</td>
<td>U.S. Geological Survey</td>
</tr>
<tr>
<td>USPS</td>
<td>U.S. Postal Service</td>
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<tr>
<td>WMO/GAW</td>
<td>World Meteorological Organization/Global Atmospheric Watch</td>
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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 precision and bias 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 high-quality data for the data user. The QAP defines these quality indicators and indicates how they are to be monitored and quantified. 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 QAP that follows contains the minimum requirements for the laboratory providing service to the program. 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. The CAL data quality objectives (DQOs) and the analytical techniques and the corrective actions for each stage of sample analysis are included in the laboratory QAP.

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 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 QA Plan (revised), 1991
- CAL QAP, 1993
- AIRMoN-wet QAP, 1995
- CAL SOPs
- CAL Statement of Work, 2001

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.

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.
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 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 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 QA Specialist 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
Environmental Health and 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 1772 ft². See Appendix B for laboratory floor plans. Total square footage for CAL offices and data management is approximately 4,304 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: PREP-01.5, PREP-04.5, PREP-54.2, DATA-01.04, and DATA-51.01.

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 one month 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) atomic absorption 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)

<table>
<thead>
<tr>
<th>Type</th>
<th>Sample volume (Vol)</th>
<th>Prioritization of chemical measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>WI</td>
<td>$10 \text{ mL} \leq \text{ Vol} &lt; 35 \text{ mL}$</td>
<td>As volume permits: pH and conductance; $\text{NH}_4^+$ and $\text{PO}_4^{3-}$; $\text{Cl}^-$, $\text{NO}_3^-$, and $\text{SO}_4^{2-}$; and $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Na}^+$, and $\text{K}^+$ until there is no more sample. If all components are measured the sample is a ‘W’ (see below).</td>
</tr>
<tr>
<td>W</td>
<td>$\text{ Vol} \geq 35 \text{ mL}$</td>
<td>Start with pH and conductance; $\text{NH}_4^+$, $\text{PO}_4^{3-}$, $\text{Cl}^-$, $\text{NO}_3^-$, $\text{SO}_4^{2-}$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, $\text{Na}^+$, and $\text{K}^+$ in that order.</td>
</tr>
<tr>
<td>DF</td>
<td>Field Blank - bucket component</td>
<td>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).</td>
</tr>
<tr>
<td>DK</td>
<td>Field Blank - bottle component</td>
<td>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).</td>
</tr>
<tr>
<td>D</td>
<td>$0 \text{ mL} \leq \text{ Vol} &lt; 10 \text{ mL}$</td>
<td>No sample shipped.</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Type</th>
<th>Sample volume (Vol)</th>
<th>Prioritization of chemical measurements</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>$\text{ Vol} \leq 10 \text{ mL}$</td>
<td>As volume permits: first pH and then conductance on unfiltered sample.</td>
</tr>
<tr>
<td>WA</td>
<td>$10 \text{ mL} &lt; \text{ Vol} &lt; 35 \text{ mL}$</td>
<td>pH and conductance on unfiltered aliquot; all other ions on filtered sample after dilution with 50 mL deionized water to provide adequate sample for analyses; measured concentrations are subsequently corrected for dilution.</td>
</tr>
<tr>
<td>W</td>
<td>$\text{ Vol} \geq 35 \text{ mL}$</td>
<td>pH and conductance on unfiltered aliquot; all other ions on filtered aliquot.</td>
</tr>
<tr>
<td>D</td>
<td>$\text{ Vol} = 0 \text{ mL}$</td>
<td>No analysis is performed, but buckets are checked for contamination and integrity.</td>
</tr>
<tr>
<td>Archive</td>
<td>$\text{ Vol} &gt; 120 \text{ mL}$</td>
<td>Two 60-mL filtered aliquots are saved. One 60-mL aliquot, ‘W’, is stored at room temperature for cation and anion measurements. One 60-mL aliquot, archive sample, is stored in a refrigerator.</td>
</tr>
</tbody>
</table>
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, refer to SOPs PREP-04.5, PREP-03.5, and PREP-54.2.

### 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: SOPs AA-01.5, FIA-01.5 (NH₄⁺), FIA-02.5 (PO₄³⁻), IC-01.5, PH-01.5, and COND-01.5. See Appendix A for more information. 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. The following 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. 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 allowable bias 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.

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.
<table>
<thead>
<tr>
<th>Type of Equipment</th>
<th>Model</th>
<th>Purchased</th>
<th>Analytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ion chromatography, conductivity detection</td>
<td>2 Dionex Model DX-500s</td>
<td>December 1994</td>
<td>Cl\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, SO\textsubscript{4}\textsuperscript{2-}</td>
</tr>
<tr>
<td>Flow injection analyzer</td>
<td>Lachat Instruments</td>
<td>October 1996</td>
<td>NH\textsubscript{4}\textsuperscript{+}, PO\textsubscript{4}\textsuperscript{3-}</td>
</tr>
<tr>
<td>Atomic absorption spectrophotometer</td>
<td>Varian, Spectra AA800</td>
<td>October 1992</td>
<td>Na\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, Ca\textsuperscript{2+}</td>
</tr>
<tr>
<td>pH meter</td>
<td>Corning 445</td>
<td>June 1998</td>
<td>pH</td>
</tr>
<tr>
<td>pH meter</td>
<td>Corning 445</td>
<td>April 2000</td>
<td>pH</td>
</tr>
<tr>
<td>Conductivity meter</td>
<td>YSI 3200</td>
<td>August 2000</td>
<td>Specific conductance</td>
</tr>
</tbody>
</table>
**Table 4. CAL Analytical Methods**

*Calcium, Magnesium, Sodium, and Potassium*


*Ammonium*

*Orthophosphate*

*Chloride, Nitrate, and Sulfate*


*pH*
Illinois State Water Survey, NADP CAL SOP PH-01.5, The Determination of pH.


*Conductivity*

*Other*

Figure 2. Sample analysis flowchart, NTN
Figure 3. Sample analysis flowchart, AIRMoN-wet
Table 5. Historical Method Detection Limits (MDLs) for Precipitation Analysis

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Field Sampling Dates</th>
<th>Lab ID Sequence (LABNO)</th>
<th>Method Detection Limit (MDL) (mg/L)</th>
<th>Analytical Methodology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>Jul 78 - Dec 78</td>
<td>NA0001 - NA0221</td>
<td>0.01</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td></td>
<td>Dec 78 - Jan 79</td>
<td>NA0222 - NA0335</td>
<td>0.02</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
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<tr>
<td></td>
<td>Jan 79 - Apr 79</td>
<td>NA0336 - NA0668</td>
<td>0.01</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td></td>
<td>Apr 79 - Aug 80</td>
<td>NA0669 - NA3361</td>
<td>0.02</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td></td>
<td>Aug 80 - Sep 80</td>
<td>NA3362 - NA3695</td>
<td>0.008</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
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<tr>
<td></td>
<td>Sep 80 - Oct 80</td>
<td>NA3696 - NA4254</td>
<td>0.006</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td></td>
<td>Oct 80 - Apr 81</td>
<td>NA4255 - NA6328</td>
<td>0.008</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td></td>
<td>Apr 81 - May 81</td>
<td>NA6329 - NA6543</td>
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</tr>
<tr>
<td></td>
<td>May 81 - Dec 01</td>
<td>NA6544 - NW0218</td>
<td>0.009</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td>Magnesium</td>
<td>Jul 78 - Apr 81</td>
<td>NA0001 - NA6328</td>
<td>0.002</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td></td>
<td>Apr 81 - May 81</td>
<td>NA6329 - NA6543</td>
<td>0.009</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td></td>
<td>May 81 - Jul 81</td>
<td>NA6544 - NA7299</td>
<td>0.002</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td></td>
<td>Jul 81 - Dec 01</td>
<td>NA7300 - NW0218</td>
<td>0.003</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td>Sodium</td>
<td>Jul 78 - Aug 80</td>
<td>NA0001 - NA3475</td>
<td>0.004</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td></td>
<td>Aug 80 - Aug 81</td>
<td>NA3476 - NA7741</td>
<td>0.002</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td></td>
<td>Aug 81 - Dec 01</td>
<td>NA7742 - NW0218</td>
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<tr>
<td>Potassium</td>
<td>Jul 78 - Jan 79</td>
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<td>0.002</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
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<tr>
<td></td>
<td>Jan 79 - Feb 79</td>
<td>NA0336 - NA0446</td>
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<td>Flame Atomic Absorption Spectrophotometry</td>
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<td>Feb 79 - Sep 79</td>
<td>NA0447 - NA1331</td>
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</tr>
<tr>
<td></td>
<td>Sep 79 - Nov 79</td>
<td>NA1332 - NA1675</td>
<td>0.004</td>
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<td></td>
<td>Nov 79 - Dec 79</td>
<td>NA1676 - NA1800</td>
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<tr>
<td></td>
<td>Dec 79 - Aug 80</td>
<td>NA1801 - NA3475</td>
<td>0.004</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td></td>
<td>Aug 80 - Apr 81</td>
<td>NA3476 - NA6000</td>
<td>0.002</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td></td>
<td>Apr 81 - Dec 01</td>
<td>NA6001 - NW0218</td>
<td>0.003</td>
<td>Flame Atomic Absorption Spectrophotometry</td>
</tr>
<tr>
<td>Analyte</td>
<td>Field Sampling Dates</td>
<td>Lab ID Sequence (LABNO)</td>
<td>Method Detection Limit (MDL) (mg/L)</td>
<td>Analytical Methodology</td>
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<tr>
<td>--------------------</td>
<td>----------------------</td>
<td>-------------------------</td>
<td>-----------------------------------</td>
<td>------------------------------------------------------------</td>
</tr>
<tr>
<td>Ammonium</td>
<td>Jul 78 - Oct 78</td>
<td>NA0001 - NA0104</td>
<td>0.03</td>
<td>Phenate (Segmented Flow Colorimetry)</td>
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<tr>
<td></td>
<td>Oct 78 - Apr 81</td>
<td>NA0105 - NA6000</td>
<td>0.02</td>
<td>Phenate (Segmented Flow Colorimetry)</td>
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<tr>
<td></td>
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<td>NA6001 - NA6650</td>
<td>0.01</td>
<td>Phenate (Segmented Flow Colorimetry)</td>
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<td>May 81 - Jun 89</td>
<td>NA6651 - NH6700</td>
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<td>Phenate (Segmented Flow Colorimetry)</td>
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<tr>
<td></td>
<td>Jun 89 - Dec 01</td>
<td>NH6701 - NW0218</td>
<td>0.02</td>
<td>Phenate (Flow Injection Colorimetry)</td>
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<td></td>
</tr>
<tr>
<td>Chloride</td>
<td>July 78 - Apr 81</td>
<td>NA0001 - NA6000¹</td>
<td>0.05</td>
<td>Ferricyanide (Segmented Flow Colorimetry)</td>
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<tr>
<td></td>
<td>Apr 81 - Apr 85</td>
<td>NA6001 - ND1937</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Apr 85 - Dec 99</td>
<td>ND1938 - NS3700</td>
<td>0.03</td>
<td>Ion Chromatography</td>
</tr>
<tr>
<td></td>
<td>Jan 00 - Dec 01</td>
<td>NS3701 - NW0218</td>
<td>0.005</td>
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</tr>
<tr>
<td>Nitrate + Nitrite</td>
<td>Jul 78 - Oct 78</td>
<td>NA0001 - NA0080</td>
<td>0.03</td>
<td>Cadmium Reduction (Segmented Flow Colorimetry)</td>
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<td>Oct 78 - Apr 85</td>
<td>NA0081 - ND1938</td>
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<td></td>
</tr>
<tr>
<td>Nitrate</td>
<td>Apr 85 - Dec 99</td>
<td>ND1939 - NS3700</td>
<td>0.03</td>
<td>Ion Chromatography</td>
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<tr>
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<td>Jan 00 - Dec 01</td>
<td>NS3701 - NW0218</td>
<td>0.010</td>
<td></td>
</tr>
<tr>
<td>Sulfate</td>
<td>Jul 78 - Apr 85</td>
<td>NA0001 - ND1938²</td>
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<td>Methylthymol Blue (Segmented Flow Colorimetry)</td>
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<td>Apr 85 - Dec 99</td>
<td>ND1939 - NS3700</td>
<td>0.03</td>
<td>Ion Chromatography</td>
</tr>
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<td></td>
<td>Jan 00 - Dec 01</td>
<td>NS3701 - NW0218</td>
<td>0.010</td>
<td></td>
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<tr>
<td>Orthophosphate</td>
<td>Jul 78 - Oct 78</td>
<td>NA0001 - NA0067</td>
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<td>Oct 78 - Feb 79</td>
<td>NA0068 - NA0452</td>
<td>0.004</td>
<td>(Segmented Flow Colorimetry)</td>
</tr>
<tr>
<td></td>
<td>Feb 79 - Apr 85</td>
<td>NA0453 - ND2633</td>
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<td>Ascorbic Acid Reduction</td>
</tr>
<tr>
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<td>Apr 85 - Jun 87</td>
<td>ND2634 - NF4630³</td>
<td>0.01</td>
<td>(Segmented Flow Colorimetry)</td>
</tr>
<tr>
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<td>Jun 87 - Nov 93</td>
<td>NF4631 - NM6824⁴</td>
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<td>Ion Chromatography</td>
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<td></td>
<td>Nov 93 - Dec 99</td>
<td>NM6825 - NS3700</td>
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<td>Ascorbic Acid Reduction (Flow Injection Colorimetry)</td>
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<td></td>
<td>Jan 00 - Dec 00</td>
<td>NS3700 - NU7202</td>
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<td>Ascorbic Acid Reduction (Flow Injection Colorimetry)</td>
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<td></td>
<td>Jan 01 - Dec 01</td>
<td>NU7202 - NW0218</td>
<td>0.009</td>
<td></td>
</tr>
</tbody>
</table>

**Notes:**

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

2 Sample NB1415 had a detection limit of 0.060 mg SO₄²⁻/L, and samples NB2015 and NB2254 had detection limits of 0.050 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.
Samples with specific conductance of 10-100 μS/cm, ± 10 percent allowable bias and ±3 percent allowable precision.

Samples with specific conductance of greater than 100 μS/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 flame atomic absorption spectrophotometry (AA), flow injection colorimetry (FIA), and ion chromatography (IC). The standard levels used are based on approximately the fifth 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 99 percentile standard, one that is within the instruments dynamic range, must be used for the highest standards. Where possible, though, 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 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. 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 appropriate SOPs).

The frequency of standardization may vary with the measurement but is not less than once per analysis day.

5.0 Record Archives

All CAL log books are kept permanently.
Table 6. Percentile Concentration Values of Chemical and Physical Parameters Measured in NADP/NTN Precipitation Wet-only Samples, 1995 - 2000

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Minimum</th>
<th>$5^{th}$</th>
<th>$10^{th}$</th>
<th>$25^{th}$</th>
<th>$50^{th}$</th>
<th>$75^{th}$</th>
<th>$90^{th}$</th>
<th>$95^{th}$</th>
<th>$99^{th}$</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcium</td>
<td>MDL</td>
<td>0.016</td>
<td>0.024</td>
<td>0.049</td>
<td>0.111</td>
<td>0.249</td>
<td>0.512</td>
<td>0.779</td>
<td>1.825</td>
<td>61.680</td>
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<tr>
<td>Magnesium</td>
<td>MDL</td>
<td>0.003</td>
<td>0.005</td>
<td>0.010</td>
<td>0.021</td>
<td>0.043</td>
<td>0.081</td>
<td>0.123</td>
<td>0.288</td>
<td>3.880</td>
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<tr>
<td>Sodium</td>
<td>MDL</td>
<td>0.009</td>
<td>0.014</td>
<td>0.029</td>
<td>0.060</td>
<td>0.140</td>
<td>0.338</td>
<td>0.613</td>
<td>2.106</td>
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<tr>
<td>Potassium</td>
<td>MDL</td>
<td>MDL</td>
<td>0.004</td>
<td>0.009</td>
<td>0.018</td>
<td>0.036</td>
<td>0.069</td>
<td>0.105</td>
<td>0.277</td>
<td>5.870</td>
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<tr>
<td>Ammonium</td>
<td>MDL</td>
<td>MDL</td>
<td>0.03</td>
<td>0.08</td>
<td>0.21</td>
<td>0.43</td>
<td>0.73</td>
<td>0.99</td>
<td>1.70</td>
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<td>Sulfate</td>
<td>MDL</td>
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<td>0.227</td>
<td>0.510</td>
<td>1.050</td>
<td>1.890</td>
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<td>3.900</td>
<td>6.360</td>
<td>125.480</td>
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<tr>
<td>Nitrate</td>
<td>MDL</td>
<td>0.180</td>
<td>0.290</td>
<td>0.590</td>
<td>1.100</td>
<td>1.870</td>
<td>2.909</td>
<td>3.790</td>
<td>6.190</td>
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<td>Chloride</td>
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<td>0.570</td>
<td>1.050</td>
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<td>Orthophosphate</td>
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<td>MDL</td>
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<td>pH (units)</td>
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<td>5.85</td>
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<td>6.77</td>
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<tr>
<td>Conductivity</td>
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<td>1.3</td>
<td>3.3</td>
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<td>7.4</td>
<td>12.6</td>
<td>21.5</td>
<td>33.6</td>
<td>43.3</td>
<td>70.0</td>
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</tbody>
</table>

Notes: Number of samples = 42,240. Mean sample volume = 1527.6 mL. Median sample volume = 959.8 mL. Maximum sample volume = 14,756.0 mL. Minimum sample volume = 24.4 mL. The Method Detection Limit changed during this six-year period (see Table 5).
Digital analytical records are maintained for five years following date of analysis. Paper records for analyses not digitally saved, i.e., the AA data, must be retained for five years. All other paper copies of analyses records must be kept for two years after transmittal to the PO.

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 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.

- 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 synthetic precipitation samples that approximate the 25th and 75th percentile concentration levels for NADP/NTN samples (FR25 and FR75) and DI water through them to check for sorption and/or leaching contaminants.
- The solutions are analyzed, and recovery percentages are calculated.
- 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.

Records of all QC data must be maintained at each work station.

The analyst initials and dates the QC data notebooks.

The CAL QA Specialist reviews QC data notebooks periodically.

Analysts generate control charts of the data daily. Analysts use 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 2.4 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, obtained from a commercial source; DI water from Room 302; and a low ionic strength synthetic rain sample prepared in house.
Each week synthetic rain samples and either the DI water or the in-house prepared sample are poured into 60-mL HDPE analysis bottles.

Samples are not filtered.

The site identification code for these samples is SWS1 (synthetic rain) and SWS2 (DI water or QC sample).

The third sample, SWS3, is the same solution as the SWS1 or SWS2 sample for that week, but it 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 sent to 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 in Building 3 of the ISWS until the data for those samples have been sent to the PO.

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 four years after data have been sent to 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 Building 3 laboratories. Once the QA report for the year is sent to the editor for final review, these samples are discarded.

11.0 Data Verification

Chemical results not captured directly by data acquisition software are entered into the data management system directly from laboratory data forms.

Keyboard data entry is stroke-verified through double entry by a second person. 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 and included in the instrument's log book. See SOPs for AA, IC, FIA, pH and specific conductance.

A record of all scheduled and unscheduled maintenance is kept.

The record 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 log.
**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.

a. Laboratory intercomparison samples of four natural rainwater or reference samples are analyzed every two weeks.

b. The USGS provides deionized water blanks to test for false positive values.

c. Currently seven laboratories participate in this program.

The CAL participates in other interlaboratory comparison programs hosted by the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW), the Canadian Centre for Inland Waters, the Acid Deposition and Oxidant Research Center, Japan (ADORC), the North Central Research Station, and the Norwegian Institute for Air Research (NILU).

On-site reviews of the CAL are conducted every three years by NADP NOS members. Review team members consist of the Subcommittee chair and others selected by the Subcommittee chair.

The review team reports results of performance and system audits to NOS. The CAL Director reports to the Subcommittee on the review team’s findings and the CAL response within six months of the review. Another NOS requirement is a paper review of the audit findings one year after the initial audit.

Reanalysis of both NTN and AIRMoN-wet samples is dependent on the number processed.

For NTN, three percent of the monthly samples are randomly selected by computer for possible reanalysis. From these samples, one third, or 1 percent of the total number of samples analyzed in that month, are randomly selected for reanalysis.

For AIRMoN-wet, 2.5 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.
Table 7. Ion Percent Difference (IPD)

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

Reanalyze if Anions + Cations < 50 µequivalents/L (µeq/L) and -60% < IPD or IPD > +60%.
Reanalyze if Anions + Cations ≥ 50 µeq/L but <100 µeq/L and -30% < IPD or IPD > +30%.
Reanalyze if Anions + Cations ≥ 100 µeq/L and -15% < IPD 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 = \((\text{H}^+)(350) + (\text{HCO}_3^-)(44.5) + (\text{Ca}^{2+})(59.5) + (\text{Cl}^-)(76.3)
+ (\text{Mg}^{2+})(53.0) + (\text{K}^+)(73.5) + (\text{Na}^+)(50.1) + (\text{NO}_3^-)(71.4) + (\text{SO}_4^{2-})(80.0) + (\text{NH}_4^+)(73.5)
+ (\text{OH}^-)(198) + (\text{PO}_4^{3-})(69.0)) ÷ 1000\) where ionic concentrations are expressed in µeq/L.

Approximately 4-6 percent of all samples are reanalyzed for AIRMoN-wet.

Not less than 1 sample in 12 is a QA sample.

2.0 Screening and Reporting Noncompliance with Data Quality Objectives

Bimonthly, the QA Specialist conducts meetings with the CAL Director, the ISWS Director of QA, the analysts, and any other interested CAL parties. 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 also provides annual QA reports of the USGS external QA programs to the PO.

The CAL QA Specialist prepares an annual QA report that discusses precision and bias and all CAL QA activities during the calendar year. Before publication, the QA report is peer reviewed by at least three scientists who are NOS members.

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 a laboratory 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 shelflife 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) contains the complete procedures for each constituent measured, including applicable range, known interferences, calculations, a statement of precision and bias, reporting units, and significant figures reported. Revised methods are implemented only with NOS approval. (Note: Methods have been modified since 1986 with the addition of new instrumentation and new computerized data acquisition systems. The basic principles of each method, however, remain the same.)

• 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), the analyst is questioned and notified in writing of the correct procedure. If the correct procedure still is not followed, the CAL Director corrects 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 there is still a problem, the CAL Director corrects the problem.

When specified equipment and supplies cannot be obtained, equivalent replacements must be located either by the QA Specialist or, more often, 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.

Sample chemical analysis for both AIRMoN-wet and NTN has protocols in place to monitor and provide input on corrective actions necessary.

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
detections 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 sees 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 C contains the current FR25, FR75, and FR25BLKS control and warning limits.

Control charts are maintained for each Quality Control Sample (QCS) solution analyte. As a minimum, a control chart is maintained for the FR25 check sample and the FR75 check sample. In addition, control charts are maintained for all standard solutions used as check samples. 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 that analyte at that concentration 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. These three lines are plotted and form the basis of the control chart. The analysts record the concentrations of each analyte for each QCS on the control chart and date the entry. The analysts initial the entry or, in a way approved by the QA Specialist, identify who has done the analyses on the control chart. Control charts are kept with the instrument in the laboratories.

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 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 overall procedure for cleaning and storing the supplies is scrutinized to determine if the contamination was external to the cleaning process. If there seems to be no obvious cause for contamination, additional buckets, lids, etc. are pulled and checked. If the same contamination appears in two consecutive blanks for two consecutive weeks, the entire cleaning process is reviewed and monitored even more closely to ensure that dirty supplies are not being shipped to 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. If, however, the reanalysis of the second replicate matches the first replicate, 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 $3\sigma$ 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, and 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, in conjunction with the ISWS QA Director 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 ACCESS 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 an RBASE relational database.

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-01.5 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-01.5, DATA-02.5, and DATA-10.5).

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-01.5 for additional details).

After double entering the FORF data, the two databases are compared and the NTN Database Manager reconciles the differences. This is completed by checking the disparate entries against the FORF data and ensuring the data in the original file are correct.

The Laboratory Observer Report Form (LORF) data are also double entered, and the two databases are compared. As with the FORF data, LORF data reconciliation is completed by checking disparate entries against the LORF data and ensuring the data in the original file are correct. This comparison is also done by the NTN Database Manager.

Chemical analysis results are loaded into the RBASE database and merged with the descriptive FORF and LORF information.
Figure 4. Sample processing and data flowchart, NTN
NOTE: Parentheses indicate table name.

Figure 4 (concluded)
Samples are loaded into the CAL database in predetermined blocks. The number of samples in a block may vary depending on the number of samples received each month from NTN sites. 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-01.5 for a complete set of checks).

The “IONBAL” program uses sample data to calculate IPD, CPD, pH, and conductivity for each wet sample. The QA Specialist uses these calculated values to select samples for reanalysis.

Preliminary data are reviewed and reported on a monthly basis for NTN.

After samples have been entered into the database, the NTN Database Manager runs a series of programs for the NTN Data Technician. The grouping of samples varies but has included up to 1200 samples and accounts for approximately four weeks of samples received at the CAL. This number can change as the number of sites either increases or decreases.

The NTN Data Technician is responsible for preliminary review of NTN data to verify data accuracy in reporting from the field sites and to apply a sampling protocol screening for each sample. Edits to the data set are based on faxes, phone calls, and notes from the sites, as well as the accuracy check. The NTN Data Technician also verifies daily precipitation amounts and reconciles those data with daily precipitation types and sampling duration (see SOP DATA-15.1 for complete details).

On or about the tenth day of each month, the NTN Data Technician gives the NTN Database Manager edits to be made to the database as a result of the data screening.

The NTN Database Manager uses appropriate programs to edit the 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-10.5).

Each month the CAL issues site-specific printouts to each NTN site operator and supervisor. These printouts include the FORF information provided by the sites with notes and error messages generated by computer programs at the CAL to provide feedback for the sites. Preliminary chemical analyses also are provided to the sites in a site-specific format. Information for facilitating ongoing communication between the sites and the CAL is included with each printout (see SOP DATA-10.5).

The CAL Administrative Assistant mails the printouts to the sites. Exact procedures may be found in the Administrative Coordinator Training Manual in room 908.

Final data review and reporting occur after completion of all other reviews.
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.

After the NTN Data Technician finishes the preliminary data review, the NTN Data Specialist takes custody of the data to conduct the final screening of the data prior to releasing the data set to the PO.

Various programs run by the NTN Database Manager facilitate this final review process (see SOP DATA-10.5).

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-19.8 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 analytes. 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 Data Specialist 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-19.8.

On or about the 20th day of each month, the NTN Data Specialist gives the NTN Database Manager edits to make to the database as a result of the data screening. The NTN Database Manager uses appropriate programs to edit the database and load edits into an edit log database (see SOP DATA-10.5).

After the edits are made, the NTN Data Specialist notifies the NTN Database Manager to copy the latest version of the databases to the PO file space and inform the PO that the new databases are available. A memo from the NTN Data Specialist to the PO contains the sample sequence, 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, an RBase relational database created in 1980. It is 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-11.1 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 which include notes pertaining to sampling gaps, site moves, siting variances, and subsampling requests.
The NTN Site Liaison has specific duties and responsibilities.

- 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 carbonless triplicate phone memos facilitates communications within the CAL to record phone conversations and convey information to the NTN Data Technician and NTN Data Specialist during the data review process. The NTN Site Liaison keeps the white copy. The pink copy is filed in the active site files. The yellow copy is retained in the archived site files if the notes contain information about sampling gaps, site moves, siting variances, and subsampling activities. All other yellow copies are recycled.

- The NTN Site Liaison also reviews each FORF for mention of equipment and collection problems (see the SOP DATA-13.5 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).

- Those e-mails from sites pertaining to data corrections are forwarded to appropriate data management staff.

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.

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

- Transmittal memos to the PO.
- Last pages of “ERRCHKK” printouts facilitate the CAL Data Specialist’s review and verification of FORF information and any changes made to the data by the CAL Data Technician (see SOP DATA 19.8).
- 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 the chemistry data for each sample (see SOP DATA-19.8 for details).

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

All correspondence with sites pertaining to data information or correction is retained for two years after transmittal to the Program Office and then discarded. Correspondence with sites concerning sampling gaps, moves, siting variances, and sub-sampling are 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 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 sample receipt observations and measurements, 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 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®. Mailers have blue or orange tape on the handle to distinguish them from NTN mailers. 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-54.1 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-54.1 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.

The AIRMoN-wet Coordinator reviews each FOF and recommends changes.

The AIRMoN-wet preliminary data review and reporting uses many of the same programs as NTN data review and reporting but modified for the AIRMoN-wet daily sampling protocols (see SOP DATA-58.1 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 are submitted electronically via the ISWS Intranet in a format ready to merge 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 and ion balance printouts.
Figure 5. Sample processing and data flowchart, AIRMoN-wet
AIRM Database

Load sample in TEMPDAT table
convert times to GMT

Load data into VALDAT table

SP/SL Coding

Load edits & run EDITVAL.DAT Program

Run AIRBAL Program

Run AIRCHK Program
(input AIRBAL.DAT & NORMALS.DAT
output QRATING.LIS)

Input QRATING.LIS to EDITS table

Run EDITVAL.DAT

Final Data Review

Data sent to Program Office

Load edits & run EDITVAL.DAT for VALDAT table edits

AIRM Database
VALDAT table

Run AIRBAL on all valid samples in VALDAT table

Run Site History
(input AIRBAL.DAT)

Update NORMALS.DAT
(run GENAIR)

Run Airanalysis Pairs Ion Balance Report

Reanalysis Review

Enter Reanalysis edits

Load samples in REANDAT table

Figure 5 (concluded)
of the analytical data for the previous month for the AIRMoN-wet Coordinator 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. Ion balance printouts contain the same information as preliminary printouts, but the data are ordered by laboratory identification number rather than by the sites. In addition, the analytical concentrations are converted to microequivalents, and pH and conductivity are calculated. The ion balance report includes the IPD and the CPD used to determine which samples may require reanalysis.

After reviewing preliminary data printouts, the AIRMoN-wet Coordinator submits a set of necessary changes for the AIRMoN-wet Database Manager to make. Revised preliminary printouts are generated for the AIRMoN-wet Coordinator.

The AIRMoN-wet Coordinator e-mails a monthly printout for review by all sites with e-mail access. Sites without e-mail receive paper copies through the U.S. Postal Service (USPS).

After site personnel receive and review the monthly preliminary data reports, they send, via e-mail when possible, any updates or corrections to the AIRMoN-wet Coordinator, 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.

The ion balance printout is reviewed to generate a list of samples for CAL reanalysis. The AIRMoN-wet Coordinator generates and distributes the reanalysis list to the AIRMoN-wet analysts.

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 delivered to the AIRMoN-wet Database Manager and loaded into the appropriate database.

Edits from the previous month are delivered to the AIRMoN-wet Database Manager and loaded in the appropriate database.

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). These files are then used to determine whether other samples from that site are contaminated. Concentrations are site dependent (see SOP DATA-58.1 for complete details).

The AIRMoN-wet Database Manager runs the “AIRCHECK” program to determine whether a sample with visible contaminants in the solution has concentrations outside the normal 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-58.1 for complete details).
The “ION BALANCE” program is run on original and reanalysis data, and the AIRMoN-wet Coordinator reviews the printout.

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 Coordinator’s final review of the FOFs (see SOP DATA-58.1 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, the FOFs, reanalysis values, and raingage charts are reviewed again.

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 transmitted to the PO.

The AIRMoN-wet Coordinator maintains all “AIRCHECK”, “PRELIMINARY DATA”, “SITE HISTORY”, “REANALYSIS”, and edit log printouts (see SOP DATA-58.1 for complete details) for the duration of the project. The “ION BALANCE” printout is maintained until the data are transferred to the PO.

The AIRMoN-wet Coordinator 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 Coordinator’s computer, which is backed up weekly.

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

For the duration of the project, all paper communications with the sites are maintained in the individual site folder maintained in the AIRMoN-wet Coordinator’s office.

The AIRMoN-wet Coordinator permanently retains all site files, including Site Visitation/Audit reports, USGS contour maps and other miscellaneous maps, Site Description Questionnaire, Site Location information, correspondence concerning site start-ups and visitations, and pictures and slides of site visitations.
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.
F. Bibliography


Appendix A

List of CAL Standard Operating Procedures (SOPs)
## CAL Standard Operating Procedures (SOPs)

**SOP #** | **Title**  
---|---  
AA-01.5 | The Determination of Calcium, Magnesium, Sodium, and Potassium by Atomic Absorption Spectrophotometry  
COND 01.5 | The Determination of Conductivity  
DATA-01.5 | Field Observer Report Form (FORF) Data Entry for the NTN  
DATA-02.5 | Laboratory Observer Report Form (LORF) Data Entry for the NTN  
DATA-10.5 | Management of the NADP/NTN/CAL Databases by the CAL Database Manager  
DATA-11.1 | Description of the CAL Site Information Database  
DATA-13.5 | Review of NTN Wet Bucket Data by the CAL Site Liaison  
DATA-15.1 | Preliminary Review of the NADP/NTN Data  
DATA-16.2 | Reanalysis Procedures for NTN and AIRMoN  
DATA-17.1 | Review of NADP/NTN Daily Precipitation Data  
DATA-19.8 | Final Review of NADP/NTN Data  
DATA-31.2 | Computer Backup and Recovery  
DATA-32.1 | Laboratory Data Management Programs  
DATA-33.1 | Archiving Laboratory Data Programs  
DATA-34.1 | Computer Programming  
DATA-35.4 | Computer Hardware and Programs, Procedures, and Software Used by the NADP/NTN/CAL Data Management Group

*Note: The alphanumeric number preceding the decimal is a unique number for each SOP and is organized by SOP type; the number after the decimal is the version number.*
CAL Standard Operating Procedures (SOPs) (concluded)

SOP #*  Title

DATA-51.2  Field Observer Form (FOF) Data Entry for the AIRMoN

DATA-54.1  Preliminary Data Management of the NADP/AIRMoN ARCHIVED

DATA-55.1  Preliminary Review of the NADP/AIRMoN Data

DATA-58.1  Data Review of the AIRMoN

FIA-01.5  The Determination of Ammonium (phenolate) by Flow Injection Analysis

FIA-02.5  The Determination of Orthophosphate by Flow Injection Analysis

IC-01.5  The Determination of Cl\(^-\), NO\(_3\)\(^-\), and SO\(_4\)\(_{2-}\) Using Dionex DX-500 Ion Chromatography

PH-01.5  The Determination of pH

PREP-01.4  Sample Preparation Laboratory Maintenance

PREP-02.5  Sample Filtration for the NTN

PREP-03.5  Bucket and Bottle Preparation

PREP-04.5  Sample Shipping and Receiving for NTN

PREP-05.4  Electrode Evaluation and Shipment

PREP-06.4  Quality Control Check Sample Preparation

PREP-07.4  Specific Conductance Standard Preparation

PREP-54.2  Sample Shipping and Receiving for the AIRMoN

QA-1.1  Quality Assurance Report

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

CAL Laboratory Floor Plans
CAL Floor Plan: Room 209
CAL Floor Plan: Building 3 (shaded areas indicate CAL laboratory space)
CAL Floor Plan: Room 302
CAL Floor Plan: Room 304

- Counter
- GAS TANKS
- Sink
- AA
- Radiator
- Clean Air Hood
CAL Floor Plan: Room 306
CAL Floor Plan: Room 323
Appendix C

Control and Warning Limits for Internally Prepared QC Solutions
Table C-1. FR25 Concentrations (mg/L), 2002

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Control (-)</th>
<th>Warning (-)</th>
<th>Mean</th>
<th>Warning (+)</th>
<th>Control (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(^{2+})</td>
<td>0.062</td>
<td>0.065</td>
<td>0.071</td>
<td>0.077</td>
<td>0.080</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>0.013</td>
<td>0.014</td>
<td>0.016</td>
<td>0.018</td>
<td>0.019</td>
</tr>
<tr>
<td>Na(^{+})</td>
<td>0.043</td>
<td>0.044</td>
<td>0.046</td>
<td>0.048</td>
<td>0.059</td>
</tr>
<tr>
<td>K(^{+})</td>
<td>0.006</td>
<td>0.008</td>
<td>0.012</td>
<td>0.016</td>
<td>0.018</td>
</tr>
<tr>
<td>NH(_4)^{+}</td>
<td>0.055</td>
<td>0.063</td>
<td>0.079</td>
<td>0.095</td>
<td>0.103</td>
</tr>
<tr>
<td>Cl(^{-})</td>
<td>0.122</td>
<td>0.125</td>
<td>0.131</td>
<td>0.137</td>
<td>0.140</td>
</tr>
<tr>
<td>NO(_3)^{-}</td>
<td>0.455</td>
<td>0.460</td>
<td>0.470</td>
<td>0.480</td>
<td>0.485</td>
</tr>
<tr>
<td>SO(_4)^{2-}</td>
<td>0.620</td>
<td>0.624</td>
<td>0.632</td>
<td>0.640</td>
<td>0.644</td>
</tr>
<tr>
<td>pH (pH units)</td>
<td>4.90</td>
<td>4.91</td>
<td>4.93</td>
<td>4.95</td>
<td>4.96</td>
</tr>
<tr>
<td>Specific Conductance (µS/cm)</td>
<td>7.1</td>
<td>7.2</td>
<td>7.3</td>
<td>7.4</td>
<td>7.5</td>
</tr>
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</table>
Table C-2. FR75 Concentrations (mg/L), 2002

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Control (-)</th>
<th>Warning (-)</th>
<th>Mean</th>
<th>Warning (+)</th>
<th>Control (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca$^{2+}$</td>
<td>0.259</td>
<td>0.266</td>
<td>0.280</td>
<td>0.294</td>
<td>0.301</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>0.059</td>
<td>0.061</td>
<td>0.065</td>
<td>0.069</td>
<td>0.071</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>0.176</td>
<td>0.181</td>
<td>0.191</td>
<td>0.201</td>
<td>0.206</td>
</tr>
<tr>
<td>K$^+$</td>
<td>0.041</td>
<td>0.044</td>
<td>0.050</td>
<td>0.056</td>
<td>0.059</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>0.325</td>
<td>0.330</td>
<td>0.340</td>
<td>0.350</td>
<td>0.355</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>0.525</td>
<td>0.530</td>
<td>0.540</td>
<td>0.550</td>
<td>0.555</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>1.912</td>
<td>1.920</td>
<td>1.936</td>
<td>1.952</td>
<td>1.960</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>2.531</td>
<td>2.547</td>
<td>2.579</td>
<td>2.611</td>
<td>2.627</td>
</tr>
<tr>
<td>pH (pH units)</td>
<td>4.32</td>
<td>4.33</td>
<td>4.35</td>
<td>4.37</td>
<td>4.38</td>
</tr>
<tr>
<td>Specific Conductance (µS/cm)</td>
<td>27.3</td>
<td>27.4</td>
<td>27.7</td>
<td>27.9</td>
<td>28.0</td>
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</tbody>
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### Table C-3. FR25 Blanks Concentrations (mg/L), 2002

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Control (-)</th>
<th>Warning (-)</th>
<th>Mean</th>
<th>Warning (+)</th>
<th>Control (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(^{2+})</td>
<td>0.059</td>
<td>0.063</td>
<td>0.070</td>
<td>0.077</td>
<td>0.081</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>0.013</td>
<td>0.014</td>
<td>0.016</td>
<td>0.018</td>
<td>0.019</td>
</tr>
<tr>
<td>Na(^{+})</td>
<td>0.040</td>
<td>0.042</td>
<td>0.046</td>
<td>0.049</td>
<td>0.051</td>
</tr>
<tr>
<td>K(^{+})</td>
<td>0.008</td>
<td>0.009</td>
<td>0.012</td>
<td>0.014</td>
<td>0.016</td>
</tr>
<tr>
<td>NH(_4)(^{+})</td>
<td>0.070</td>
<td>0.073</td>
<td>0.079</td>
<td>0.085</td>
<td>0.087</td>
</tr>
<tr>
<td>Cl(^{-})</td>
<td>0.121</td>
<td>0.123</td>
<td>0.127</td>
<td>0.131</td>
<td>0.133</td>
</tr>
<tr>
<td>NO(_3)(^{-})</td>
<td>0.450</td>
<td>0.453</td>
<td>0.459</td>
<td>0.465</td>
<td>0.468</td>
</tr>
<tr>
<td>SO(_4)(^{2-})</td>
<td>0.606</td>
<td>0.611</td>
<td>0.621</td>
<td>0.631</td>
<td>0.636</td>
</tr>
<tr>
<td>pH (pH units)</td>
<td>4.84</td>
<td>4.87</td>
<td>4.93</td>
<td>4.99</td>
<td>5.02</td>
</tr>
<tr>
<td>Specific Conductance (μS/cm)</td>
<td>6.9</td>
<td>7.0</td>
<td>7.1</td>
<td>7.2</td>
<td>7.3</td>
</tr>
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Table C-4. FR10 Blanks Concentrations (mg/L), 2002

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<tr>
<th>Parameter</th>
<th>Control (-)</th>
<th>Warning (-)</th>
<th>Mean</th>
<th>Warning (+)</th>
<th>Control (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>0.023</td>
<td>0.025</td>
<td>0.029</td>
<td>0.033</td>
<td>0.035</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.003</td>
<td>0.004</td>
<td>0.006</td>
<td>0.008</td>
<td>0.009</td>
</tr>
<tr>
<td>Na⁺</td>
<td>0.015</td>
<td>0.016</td>
<td>0.018</td>
<td>0.020</td>
<td>0.021</td>
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<tr>
<td>K⁺</td>
<td>0.000</td>
<td>0.000</td>
<td>0.004</td>
<td>0.008</td>
<td>0.010</td>
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<tr>
<td>NH₄⁺</td>
<td>0.021</td>
<td>0.023</td>
<td>0.029</td>
<td>0.035</td>
<td>0.038</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.044</td>
<td>0.047</td>
<td>0.053</td>
<td>0.059</td>
<td>0.062</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.180</td>
<td>0.184</td>
<td>0.192</td>
<td>0.200</td>
<td>0.204</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.235</td>
<td>0.242</td>
<td>0.256</td>
<td>0.270</td>
<td>0.277</td>
</tr>
<tr>
<td>pH (pH units)</td>
<td>5.13</td>
<td>5.16</td>
<td>5.23</td>
<td>5.30</td>
<td>5.34</td>
</tr>
<tr>
<td>Specific Conductance (μS/cm)</td>
<td>3.2</td>
<td>3.3</td>
<td>3.4</td>
<td>3.5</td>
<td>3.6</td>
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