NADP QA Plan 2009-01

QUALITY ASSURANCE PLAN
CENTRAL ANALYTICAL LABORATORY

National Atmospheric Deposition Program

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

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

In October 1992, the Atmospheric Integrated Research Monitoring Network (AIRMoN), currently with seven sites, joined the NADP. AIRMoN sites collect samples daily when precipitation occurs. Samples are refrigerated until analysis at the CAL for the same constituents measured in NTN samples. The AIRMoN seeks to investigate pollutant source/receptor relationships and the effect of emissions changes on precipitation chemistry, combining measurements with atmospheric models. The AIRMoN also evaluates sample collection and preservation methods.
In January 1996, the Mercury Deposition Network (MDN), currently with more than 90 sites, joined the NADP. MDN sites collect wet-only deposition samples that are sent to the MDN analytical laboratory at Frontier Geosciences, Inc. The MDN was formed to provide data on the wet deposition of mercury to surface waters, forested watersheds, and other receptors. Forty-five states and eight Canadian provinces have advisories against consuming fish from lakes with high mercury concentrations in fish tissues. MDN data enable researchers to investigate the link between mercury in precipitation and this problem.

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

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Quality Assurance Plan

Version 4.0, April, 2009

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Quality Assurance Plan Approval Form

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

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Acronyms and Abbreviations

AIRMoN	Atmospheric Integrated Research Monitoring Network
ANSI	American National Standards Institute
ASQC	American Society for Quality Control
CAL	Central Analytical Laboratory
CPD	Conductance Percent Difference
DI	Deionized
DMAS	Data Management and Assessment Subcommittee
DQOs	Data Quality Objectives
ECPTP	Environment Canada Proficiency Testing Program
FIA	Flow Injection Analysis
FOF	Field Observer Form (AIRMoN)
FORF	Field Observer Report Form (NTN)
FR25	A synthetic rainwater solution formulated to approximate the 25th percentile concentrations of the NADP/NTN
FR75	A synthetic rainwater solution formulated to approximate the 75th percentile concentrations of the NADP/NTN
HDPE	High-Density Polyethylene
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
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
NADP	National Atmospheric Deposition Program
NILU	Norwegian Institute for Air Research
NIST	National Institute for Standards and Technology
NOS	Network Operations Subcommittee
NRSP-3	National Research Support Project
NTN	National Trends Network

Acronyms and Abbreviations (concluded)

PO	Program Office
QA	Quality Assurance
QAAG	Quality Assurance Advisory Group
QA/R-5	EPA Requirements for QA Project Plans
QAP	Quality Assurance Plan
QC	Quality Control
QCS	Quality Control Standard
QMP	Quality Management Plan
Site ID	Station identification code
SL	Screening Level
SOP	Standard Operating Procedure
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
WMO/GAW	World Meteorological Organization/Global Atmospheric Watch

Quality Assurance Plan Document History

Approval Date:	August 21, 2002	
Revisions:	2.0 June 1, 2006	
	B-2.0, Table 2	Revised sample dilution procedures implemented based on Network Operations Subcommittee (NOS) 2002 audit team recommendation
	B-4.0	Revised procedure for calculating Method Detection Limits (MDLs)
	B-4.0, Table 3	Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES) replaced Atomic Adsorption Spectrometer as of January 2004. (Other changes were made throughout the document to reflect this change.)
	B-4.0, Table 5	Table of historic MDLs updated
	B-4.0, Table 6	Percentiles for concentration values updated
	B-5.0	Records retention period changed to 2.5 years after date of analysis
	C-1.0	Selection of samples for random reanalysis changed. Samples are selected automatically by the Laboratory Information Management System (LIMS) and not by the QA Specialist.
	D	Chapter revised extensively with updated flowcharts and other information to reflect functionality of LIMS system implemented since last revision
	All sections	Minor editorial changes were made throughout the document to clarify procedures.
Revisions:	3.0 April, 2008	
	B-3.0, Table 2	Revised sample volume threshold to 8.0 mL
	B-3.0, Table 3	Deleted
	B-4.0, Table 4	Deleted
	B-4.0, Table 5	Deleted
	B-4.0	Clarification of reanalysis procedures
	B-7.0	Additional high concentration QCS for ICP
	All sections	Minor editorial changes were made throughout the document to clarify procedures.
Revisions:	4.0 April 2009	
	Section C	Tables 2 and 3 (IPC and CPD) removed
	Section D	Sections 2.0 and 3.0

All sections	Minor editorial changes were made throughout the document to clarify procedures.

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 quality assured and screened data for which NADP data quality objectives 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 that data meet user needs. The QAP defines these quality indicators and specifies how they are to be monitored and quantified. This QAP is designed to cover all aspects of sample processing, sample analysis, instrument calibration, internal QC checks, data handling, data screening, and final data processing prior to data transfer to the NADP PO.

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 component (NADP/AIRMoN) and the NADP/National Trends Network (NADP/NTN) sites must follow strict quality assurance (QA) and quality control (QC) procedures. The laboratory that has provided these services to the NADP/NTN and NADP/AIRMoN is located at the Illinois State Water Survey (ISWS) in Champaign, Illinois. 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 sites. The number of sites for each network fluctuates from year to year, increasing and decreasing the sample load to the CAL.

Quality assurance for the analytical measurement process at the CAL is a multi-tiered program that includes bench-level QC, laboratory management-level QA, and participation in external QA monitoring efforts. The laboratory continually strives to improve the current methods and to find new instrumentation that will achieve lower detection limits, improve sample throughput, improve measurement precision, and reduce bias for analytical measurements. Documentation of these methods' characteristics is updated annually in the laboratory QA report. Standard Operating Procedures (SOPs) for all support activities are maintained and updated annually.[1]

The NADP/CAL QAP follows the ISWS and the NADP Quality Management Plans (QMP), the "umbrella" QA documents that describe the processes and procedures for staff and management to follow in producing environmental data. The NADP/CAL QAP 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

[1] CAL SOPs can be found at http://nadppo1.sws.uiuc.edu/ops/cal/default.aspx.

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

The following is a list of relevant source documents:

- ISWS Quality Management Plan
- NADP Quality Management Plan
- NADP QA Plan
- AIRMoN QA Plan
- CAL SOPs
- CAL Work Plan[2]

The CAL QA Chemist and the CAL Director will review this plan annually and update as needed but no less frequently than once every three years. All revisions will be numbered and dated; previous versions will be kept in the CAL archives for reference.

2.0 Management and Organization

The CAL Director reports to the NADP Program Coordinator who reports directly to the ISWS Director and is also responsible to the NADP Executive Committee. The NADP CAL Director/Assistant Coordinator is responsible for seeing that all laboratory activities follow the requirements defined in the CAL Work Plan. Figure 1 shows a current organizational chart for the NADP CAL.

The QA Chemist for the NADP CAL is responsible for monitoring the overall quality of the laboratory operations. The QA Chemist serves on the NADP's Quality Assurance Advisory Group (QAAG). The QA Chemist performs QA/QC duties as specified by this QAP and additional duties requested by the CAL Director. The QA Chemist is independent of the analysis of the samples, but is involved with troubleshooting and quality control in the laboratory. Annually, the QA Chemist writes and presents the NADP subcommittees with a detailed QA report summarizing QA activities for the preceding year.

The NADP technical staff includes scientists, permanent support staff, and hourly staff. The NADP staff is committed to continued 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.

3.0 Elements of NADP CAL Quality System

This QAP describes the day-to-day QA/QC procedures. The CAL QA Chemist is responsible for maintaining the CAL QAP. Standard Operating Procedures (SOPs) describe the detailed method for an operation, activity, or analysis so that the procedure can be performed consistently over a long time period.

[2] The CAL Work Plan is the contractual document between the CAL and the Program Office. For more information, contact the Program Coordinator or CAL Director.

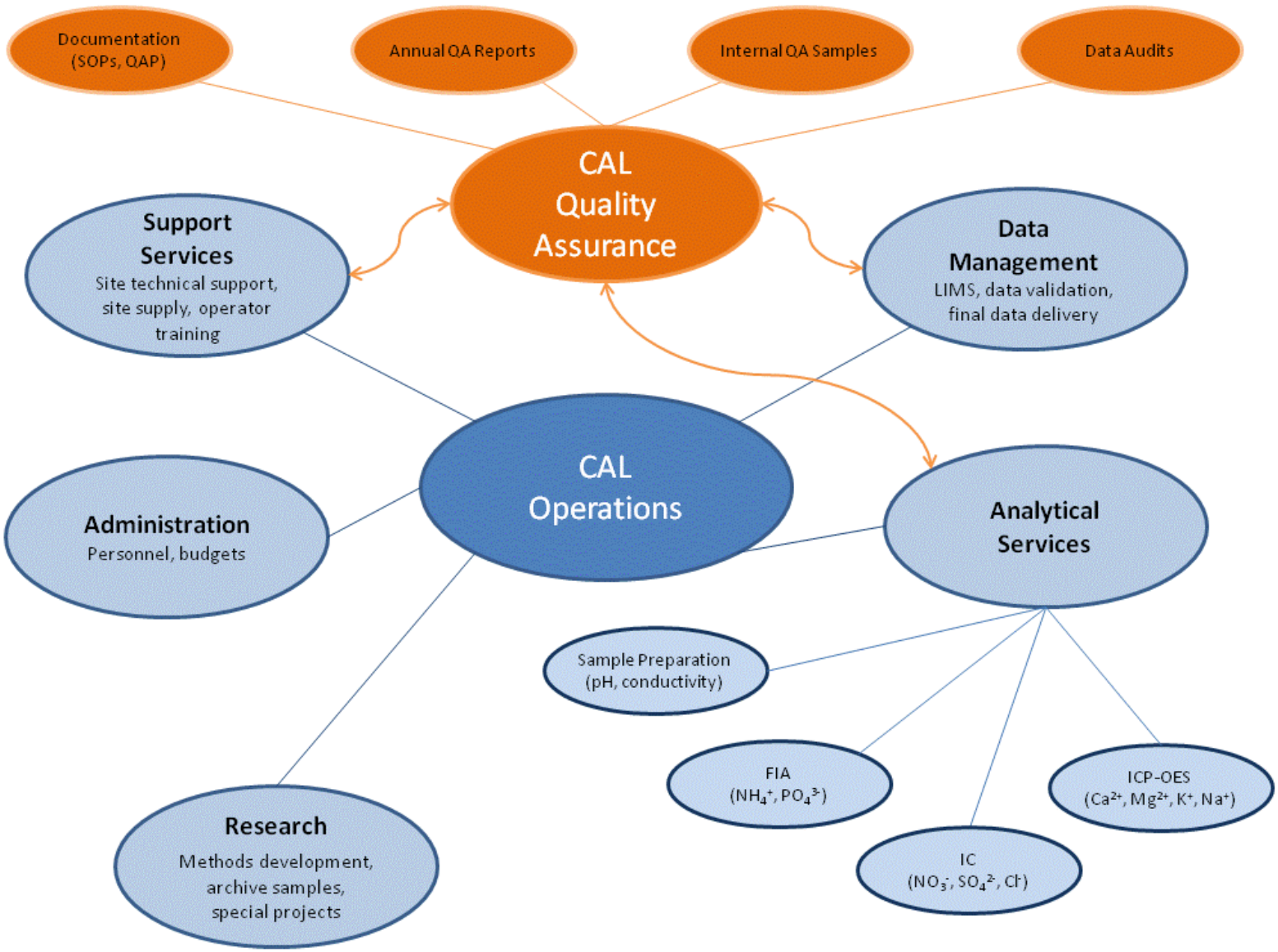

Figure 1. Central Analytical Laboratory Organizational Chart

Periodic on-site technical reviews are conducted to evaluate documents, activities, materials, data, and other work products that require technical verification for bias, precision, completeness, and representativeness. The NADP Technical Committee, under the guidance of the NOS, DMAS, and the NADP QA Manager, conducts on-site CAL technical reviews every three years with a follow-up paper review one year following the on-site review per the NADP Quality Management Plan (NADP 2003).

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 CAL Director, or QA Chemist. The CAL Director is responsible for retaining records that document review findings and responses.

4.0 Personnel Qualifications and Training

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

As a minimum requirement, new staff must be trained for specific jobs by another CAL staff member familiar with that job and may need to attend structured courses that cover specific training in instrumentation, procedures, and 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 Chemist 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. The staff is required to upgrade and expand their skills into new areas continually. 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 though the University of Illinois Division of Research Safety. All CAL staff are encouraged to participate in all safety training courses.

All 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 CAL facilities are located at the ISWS on the campus of the University of Illinois at Urbana-Champaign. Total square footage for laboratories, shipping, and receiving at the CAL is approximately 4000 ft^2.

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 is contained in SOPs for sample preparation.

As samples are logged in, information from the NTN Field Observer Report Form (FORF) or AIRMoN Field Observer Form (FOF) is entered into a Laboratory Information Management System (LIMS) and from there into the data base. Each sample is identified by a unique laboratory number (LABNO) and station identification code (Site ID). These designators remain linked to the sample throughout data verification and transfer of final data to the PO.

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

Sample processing differs for AIRMoN and NTN.

- Sample processing protocols are dependent upon sample volume. Different analysis protocols are used for AIRMoN and NTN (see Tables 1 and 2, respectively, for details.)
- Both pH and specific conductance must be measured for all samples with sufficient volume within four business days of their arrival at the CAL (AIRMoN samples) and within three business days of sample login (NTN samples).
- For AIRMoN samples, all other analyses must be completed within two weeks of their arrival at the CAL.
- For NTN samples, all other analyses must be completed within three weeks of their arrival at the CAL.
- The order for chemical analysis of AIRMoN samples is listed in Table 1. The order for chemical analyses of NTN samples is pH and conductivity first followed by the remaining analytes in no particular order.

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

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

Type	*Sample volume (Vol)*	*Prioritization of chemical measurements*
WI	10 mL ≤ Vol < 50 mL	As volume permits: pH and conductance; NH_4^+ and PO_4^{3-}; Cl^-, NO_3^-, and SO_4^{2-}; and Ca^{2+}, Mg^{2+}, Na^+, and K^+ until there is no more sample. If all components are measured the sample is a 'W' (see below).
W	Vol ≥ 50 mL	Start with pH and conductance; NH_4^+, PO_4^{3-}, Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, Na^+, and K^+ in that order.
DF	Field Blank - bucket component	Field Blank bottle sent from the CAL: half is poured into the bucket then, after at least 8 hours, is poured into a clean bottle and returned to the CAL for analysis as if it were a 'W' (see above).
DK	Field Blank - bottle component	Half of the Field Blank bottle, not poured into the sample bucket, is returned to the CAL in the original bottle, and analyzed as if it were a 'W' (see above).
D	0 mL ≤ Vol < 10 mL	No sample shipped.

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

Type	*Sample volume (Vol)*	*Prioritization of chemical measurements*
T	Vol $\leq$ 8 mL	As volume permits: first pH and then conductance on unfiltered samples.
WD	8.0 mL < Vol < 30.5 mL	pH and conductance on unfiltered aliquot; all other ions on filtered sample after dilution to a volume of 50 mL with deionized water to provide adequate sample for analyses; measured concentrations are subsequently corrected for dilution.
W	Vol $\geq$ 30.5 mL	pH and conductance on unfiltered aliquot; all other ions on filtered aliquot.
D	Vol = 0 mL	No analysis is performed.
DF	Field Blank - bucket component	U. S. Geological Survey (USGS) Field Blank bottle sent to the site 75% is poured into the bucket then, after about 24 hours, is poured into a clean sample bottle and returned to the CAL for analysis as if it were a 'W' (see above).
DK	Field Blank - bottle component	25% of the USGS Field Blank bottle, not poured into the sample bucket, is returned to the CAL in the original bottle, and analyzed as if it were a 'W' (see above).

4.0 Sample Chemical Analysis

The overall program objective is to produce analytical data for which precision and bias are quantified. DQOs are defined to optimize data quality. Information relating to NADP analytes measured, instruments used, and the dates the instruments were purchased is available at http://nadp.isws.illinois.edu. Full documentation of these instruments is maintained. Figure 2 is a flowchart for processing NTN samples. Figure 3 is a flowchart for processing AIRMoN samples.

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). The MDLs are a data quality indicator that is reviewed and revised by the QA Chemist as warranted, i.e., when a new instrument is purchased, when a critical new part is installed on an existing instrument, or when analysts start using the instruments for the first time. The MDLs are calculated at least annually as described in SOP QA-0020. The QA Chemist compiles the results from the previous 12 months data and reviews them with the CAL Director. The MDLs are updated with the PO at least once a year.

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 is determined by the analysis of routine blind samples of known concentration.

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

- A maximum allowable bias of $\pm$ 100 percent at the MDL.
- A $\pm$ 20 percent allowable bias at 10 times the MDL.
- A $\pm$ 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.
- 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.

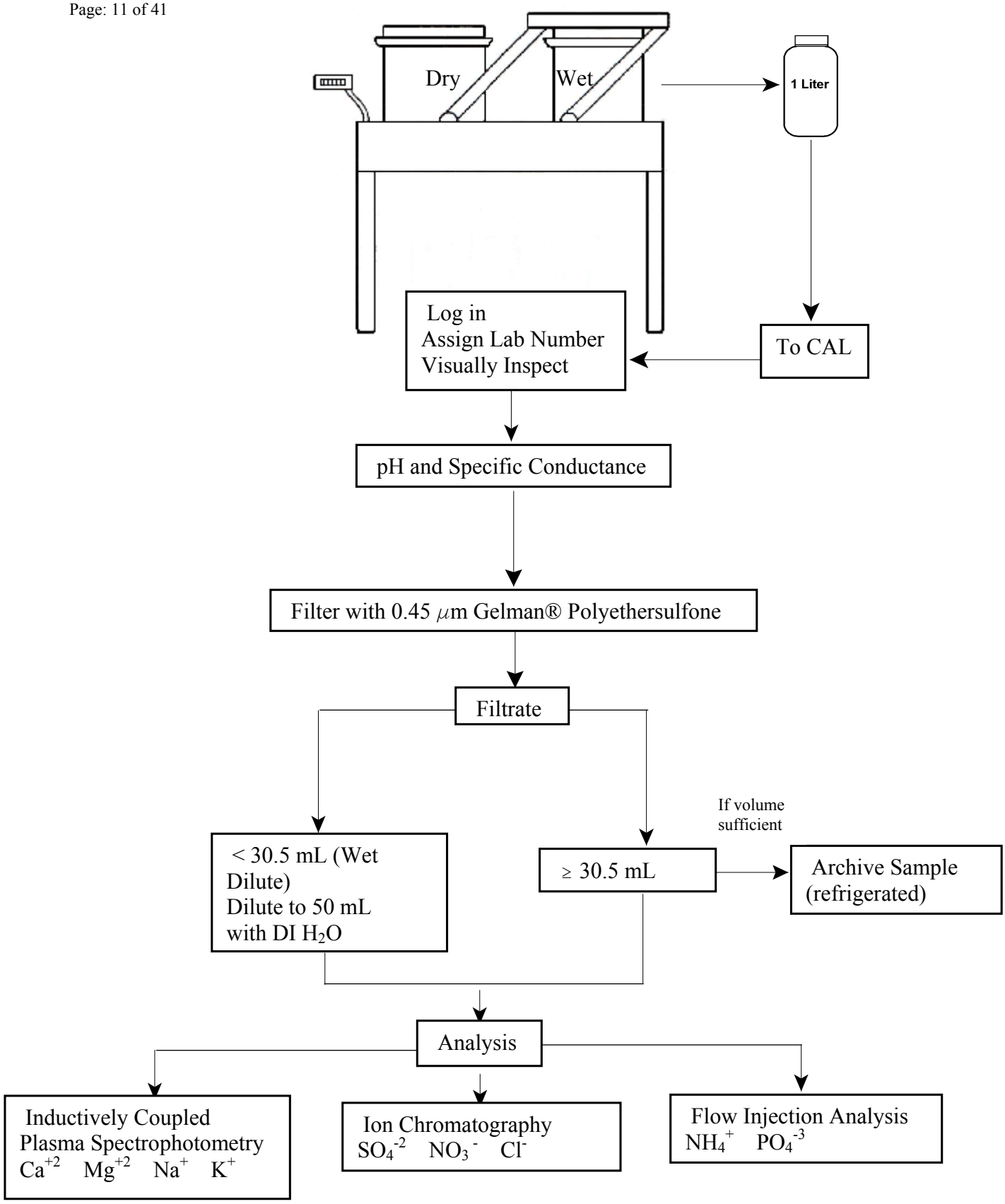

Figure 2. Sample analysis flowchart, NTN

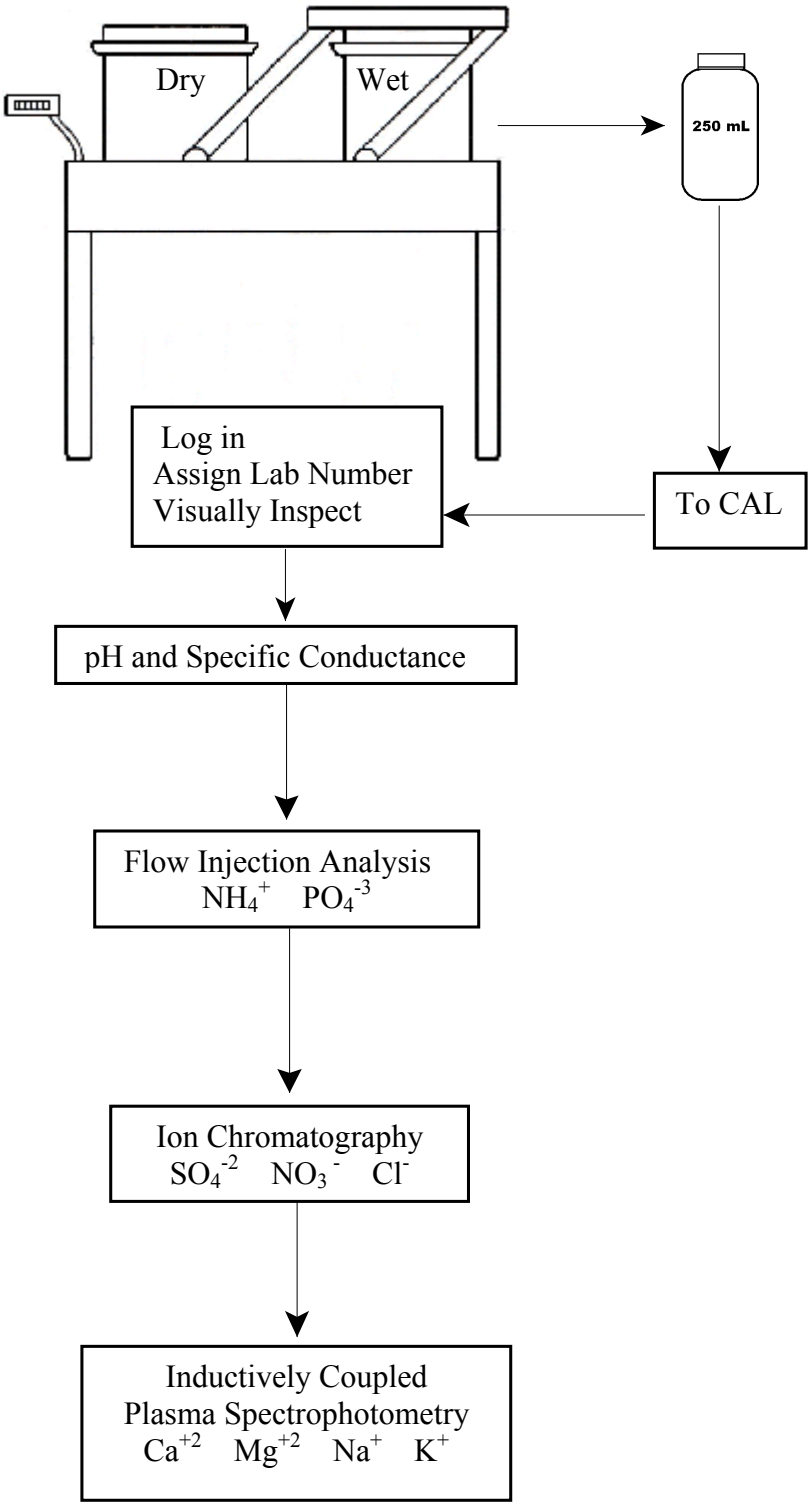

Figure 3. Sample analysis flowchart, AIRMoN

The difference allowed between the original sample analyses and replicate sample analyses or randomly selected reanalyzed sample analyses is 10 percent. If the difference between an original and a reanalysis or replicate sample is greater than 10 percent, an additional analysis of the original or replicate sample must be performed. If there is an archived sample (NTN) available this also must be analyzed. Since replicates and random reanalysis samples are analyzed to make sure that all instrumentation was working correctly and no other errors occurred during the initial analysis, it is important to confirm the concentrations obtained by reanalyzing the samples. If the difference between the original and the replicate or reanalyzed sample is real, additional samples may need to be reanalyzed to ascertain that the instruments were working correctly for samples before and after the original. Additional reanalyses will determine whether the instrument was out of control, some operational error had occurred, the original sample was possibly contaminated, or that the chemistry of the sample is changing.

Standardization is instrument specific. All instruments are standardized each day they are used. In addition, pH and specific conductance are standardized every 36 samples. A minimum of five standards is used to standardize the inductively coupled plasma-optical emission spectroscopy (ICP), flow injection colorimetry (FIA), and ion chromatography (IC). The standard levels used are based on approximately the 5^{th} percentile to the 99^{th} percentile concentrations found in the NADP/NTN data set. For some instrumentation, however, this range is too broad (FIA), resulting in the higher concentrations not being within the dynamic range of the instrument. For these analytes, a lower than 99^{th} percentile standard, one that is within the instruments dynamic range, must be used for the highest standards. Where possible, the highest standard for each analyte is near the 99^{th} 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. For the ICP, rather than diluting the sample, a broader range of standards is used. Standardization and calibration procedures are the same for AIRMoN and NTN for all instrumentation.

All primary standards must be confirmed using both of these following methods:

- Certified reference solutions or second source standards (standards made by and obtained from a different source from the primary standards) to compare with the new stock standards.
- Prior standards to compare with the new standards.

If other comparisons are done instead of the above two, they must be approved by the QA Chemist and documented in the laboratory log book and the SOP for that method. All primary standard solutions are remade or purchased a few days to a couple of weeks before the expiration date of the old solutions, allowing the analysts time to compare the new with the old and to verify the new standards are within tolerance levels. Instrument standardization procedures are documented for

each analyte. 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 permanently kept on file at the Illinois State Water Survey. Digital analytical records are maintained for a minimum of five years following date of analysis. Paper records for analyses not digitally saved must be retained for five years following date of analysis. For analytical methods with digital records and paper records, the paper records must be maintained for 2.5 years after date of analysis.

6.0 General Laboratory Procedures

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

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

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

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

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

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

- Whenever a new lot of filters is obtained, the filters are checked by passing a synthetic precipitation sample that approximates the 25th percentile concentration level for NADP/NTN samples (FR25) and DI water through them to check for sorption and/or leaching contaminants.
- The solutions are analyzed, and approved by the QA Chemist providing the concentrations of the leachates are within established control limits.
- Before a new analyst can filter samples, his/her performance will be assessed and validated by monitoring QC samples to check his/her filtering technique.

- If the concentrations of the solutions used are within the standard control limits for those solutions, the QA Chemist approves the use of the new lot of filters or approves the performance of the analyst.

7.0 Instrument Procedures

A high and a low quality control sample (QCS) are analyzed immediately after standardization to ensure that the system is in control. At a frequency of not less than one sample in 12, at least two of the following checks should be made:

- QCS[1]
- High Standard (not used for calibration)
- Low Standard (not used for calibration)

All QC data are recorded directly from the analytical instruments into the LIMS. Control charts of the data are automatically generated in the LIMS as soon as data transfer is complete. Analysts use the control charts to determine the condition of their analytical systems, i.e., in control, drifting, or biased.

The analytical and pan balances are monitored for proper operation and accuracy by using National Institute for Standards and Technology (NIST) 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

Supplies used at CAL are routinely checked for contamination. These supplies include, but are not limited to:

- Collection buckets and lids
- NTN and AIRMoN shipping bottles
- DI water
- Filter blanks
- Bucket and lid storage bags
- NTN sample bottles

Procedures for these checks are described in SOP PR-0041.

9.0 Sample Precision

Replicate analyses are performed on approximately one percent of the NADP/AIRMoN and 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

[1] For the ICP, a high concentration QCS may be used instead of one of the original QCSs used if there is a sample in the set of 12 that is of high concentration, providing the standardization curve covers the higher concentration.

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. One QC sample per week is introduced into the analytical queue each month disguised as real precipitation samples for AIRMoN and three samples per week for NTN, for a total of four blind QC samples per week. Complete details are in SOP QA-0049.

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 Chemist 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 samples must be stored at 4^{o}C. These samples are kept at the CAL for two years after finalized data have been published by the PO.

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

External intercomparison samples are stored at 4^{o}C. All USGS intercomparison samples and blank samples are stored in the laboratories during processing. Upon completion of the analysis, the samples are stored in the NTN archive sample refrigerator until the QA Chemist has reviewed the results, after which these samples are discarded.

11.0 Data Verification

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

Computer programs contain control checks for data entry. An ion percent difference (IPD) is calculated for each sample. The conductance percent difference (CPD) between calculated and measured specific conductance is tabulated (for information on the IPD and CPD see SOP #DA-0067.0). Samples are randomly selected for reanalysis for both AIRMoN and NTN to verify sample concentrations (see Section C “Laboratory QA/QC Procedures” for more information).

12.0 Preventive Maintenance/Service

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

C. Laboratory QA/QC Procedures

1.0 Performance and Systems Audits

The CAL participates in several formal external QA programs.

The USGS administers the Interlaboratory Comparison Program for NADP/NTN. Laboratory intercomparison samples of four natural rainwater, deionized water, or reference samples are analyzed every month. Refer to USGS webpage (http://bqs.usgs.gov/precip/interlab_overview.htm) for more information.

The CAL participates in other interlaboratory comparison programs such as those hosted by the World Meteorological Organization/Global Atmospheric Watch (WMO/GAW), the Environment Canada Proficiency Testing Program (ECPTP), and the Norwegian Institute for Air Research (NILU).

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

Reanalysis of both NTN and AIRMoN samples is dependent on the number of samples processed. For NTN, one percent of the total number of samples analyzed during the week is selected randomly for reanalysis. For AIRMoN, two percent of the samples are selected randomly for reanalysis. Samples also are selected for reanalysis if they exceed the predetermined control limits for ion balance and specific conductance differences. See SOP DA-0067.0 for the Ion Percent Difference (IPD) and Conductance Percent Difference (CPD) reanalysis criteria. Approximately two to six percent of all samples are reanalyzed for NTN. Approximately four to six percent of all samples are reanalyzed for AIRMoN.

2.0 Screening and Reporting Noncompliance with Data Quality Objectives

Bimonthly, the CAL QA Chemist conducts QA meetings with the CAL staff. These meetings include discussions of the results and evaluation of internal QA program analyses and of any current laboratory conditions. Use of control charts, improvement of analyses, and any proposed method changes also are discussed.

The USGS provides annual QA reports of the USGS external QA programs (interlaboratory comparison program and the NTN field blank program) to the PO. The CAL QA Chemist prepares an annual summary that discusses and reports overall laboratory data quality as well as all CAL QA activities during the calendar year. Before publication, the CAL QA report is peer reviewed and sent to the ISWS editor.

Documents required to support the QC/QA activities of the analytical laboratory consist of log books, SOPs, and this CAL QAP.

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

3.0 Corrective Actions

Depending on the analytical or CAL procedure, different corrective actions must be followed. For example, shipping and receiving is handled differently than the analytical processes in the laboratory. However, each process is important and has specific corrective actions for noncompliance. It is the QA Chemist'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 and NTN. SOPs are in place for all sample chemical analyses for both AIRMoN and NTN. These SOPs contain detailed information on analytical problems to avoid and suggestions for corrective actions when problems occur.

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) or within 72 hours of sample log-in (NTN), staff are alerted and notified in writing of the correct procedure. If the correct procedure still is not followed, the CAL Director implements system changes to correct the problem.

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

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

Analytical methods used by the CAL must not change without approval from NOS. 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 Chemist contacts the analyst to check data for accuracy and for transcription errors. If this is not the problem, or if the system was out of control (analytical check samples were not within specified control limits) during the analytical process, the analyst is asked to reanalyze the samples. The CAL Director is notified of the problem and ensures that corrective action has been taken.

If the standards used have not been confirmed using both 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 Quality Control Samples (QCS) 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). QCS are prepared annually and may vary slightly from the target concentrations.

Control charts are automatically generated for each QCS solution analyte with the LIMS. The true or expected value of each analyte for each solution is determined before the sample is used as a QCS. The warning limit for each analyte and each control solution is determined as two times the standard deviation found by 7-10 replicate analyses of the solution. The control limit is three times the standard deviation. The warning and control limits are plotted and form the basis of the control charts. The LIMS updates the control charts each time the analysts send data to the LIMS The date of the analysis is also recorded on the control chart in the LIMS. The LIMS maintains a record of the analyst operating the instruments each day.

If any single measurement of a reference sample measured to verify correct operation is outside the control limits (3σ), all analyses of samples ceases and corrective action is taken. If the instrument cannot 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. These situations indicate serious problems with the system and must be addressed by the analyst. The analyst, with the help of the QA Chemist and the CAL Director as needed, determines the corrective action to be taken.

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

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

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

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

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

If any buckets, lids, or bottles selected for random contamination checks are determined to be contaminated, the contaminated bucket, lid, or bottle is visually inspected to ascertain if the contamination is obvious as not being thoroughly cleaned. If the bucket, lid, or bottle is severely contaminated or the structural integrity of the bucket, lid, or bottle is compromised, the bucket, lid, or bottle is discarded. If there is no physical evidence of contamination, the bucket, lid, or bottle is rechecked to verify that the contamination was in the bucket, lid, or bottle not contaminated during analysis and handling of the sample. If the bucket, lid, or bottle is still contaminated, it is rewashed and rechecked. If it is still contaminated, it is discarded. If the supplies are consistently contaminated, the overall procedure for cleaning and storing the supplies is scrutinized to

determine if the contamination was external or internal to the cleaning process. If there seems to be no obvious cause for contamination, additional buckets, lids, etc., are pulled and checked. If need be, the entire cleaning process is reviewed to determine if the SOPs are being followed, if the washer needs to be cleaned more frequently, if there are contaminants present in the wash room, if handling protocols are being followed, or if protocol changes are needed, in an attempt to ensure clean supplies for the sites.

If the difference between the replicate samples processed randomly during analysis or reanalysis is greater than 10 percent, the replicate and/or the original sample must be reanalyzed. If the original now matches the replicate, then the analyst must determine what or if there was an error in the original analysis and if so, did that error affect any other samples. All samples affected must be reanalyzed and the data base corrected. If the replicate still differs by more than 10 percent, the analysts must try to determine if either the original or replicate sample was contaminated or was chemically changing. If no obvious error during analysis is found, the samples analyzed adjacent to the replicate may need to be reanalyzed to ensure that the problem was unique to the one sample.

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

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

For reanalysis samples, if differences are found between the original analytical data and the randomly chosen samples for reanalysis, no data correction can be made unless it can be proven that there was an error in the original analyses. If there is an error, samples adjacent to the randomly chosen sample must be checked and reanalyzed to ensure that the problem did not exist for adjacent samples. Samples that are identified for reanalysis due to IPD or CPD must be checked carefully to ensure that if there is a real, statistical difference in analytical results between the original sample and the reanalysis sample, that the difference is the result of an analytical error, not the result of the sample changing over time. If there is a contaminant in the sample, the degree of contamination is important in evaluating the reanalysis concentrations. Only with written justification and authorization by the QA Chemist, 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 Chemist.

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 Chemist. The CAL QA Chemist 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 Management Committee and the Computer Services Coordinator should be consulted when selecting computer hardware.

Computer software should be purchased from an approved University of Illinois 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. Typically, this would involve running old and new versions of programs in parallel (where appropriate), to ensure that consistent results are obtained. Manual calculations must be conducted on test data sets to confirm the reliability of the software prior to routine use. Such calculations should be reviewed and/or replicated by a third person or party other than those involved in developing the programs.

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 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 NTN SQL server relational database is the primary database used for this purpose.

When the precipitation sample and FORF are received at the CAL, the white copy is separated from the yellow copy, and the raingage chart, as appropriate, is stapled to the yellow copy. All information on the FORF is typed into the LIMS; electronic raingage data are imported when available.

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 DA-1030 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 DA-1030, and DA-0037).

During FORF sorting and screening, sample receiving personnel identify certain problems that require e-mailing or faxing the sites for clarification. This procedure has helped to facilitate faster resolution of FORF errors or incomplete information (see SOP DA-1030 for additional details).

FORF data and chemical analysis results are loaded from the LIMS into the NTN SQL database when final analyses are complete. Samples are loaded weekly with the number of samples dependent upon laboratory results.

A reanalysis ion balance is run on reanalysis pairs. Percentage differences between original and reanalysis values are calculated as part of this procedure. Differences greater than 10 percent are identified. 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 QA Chemist recommends changing the original values to the

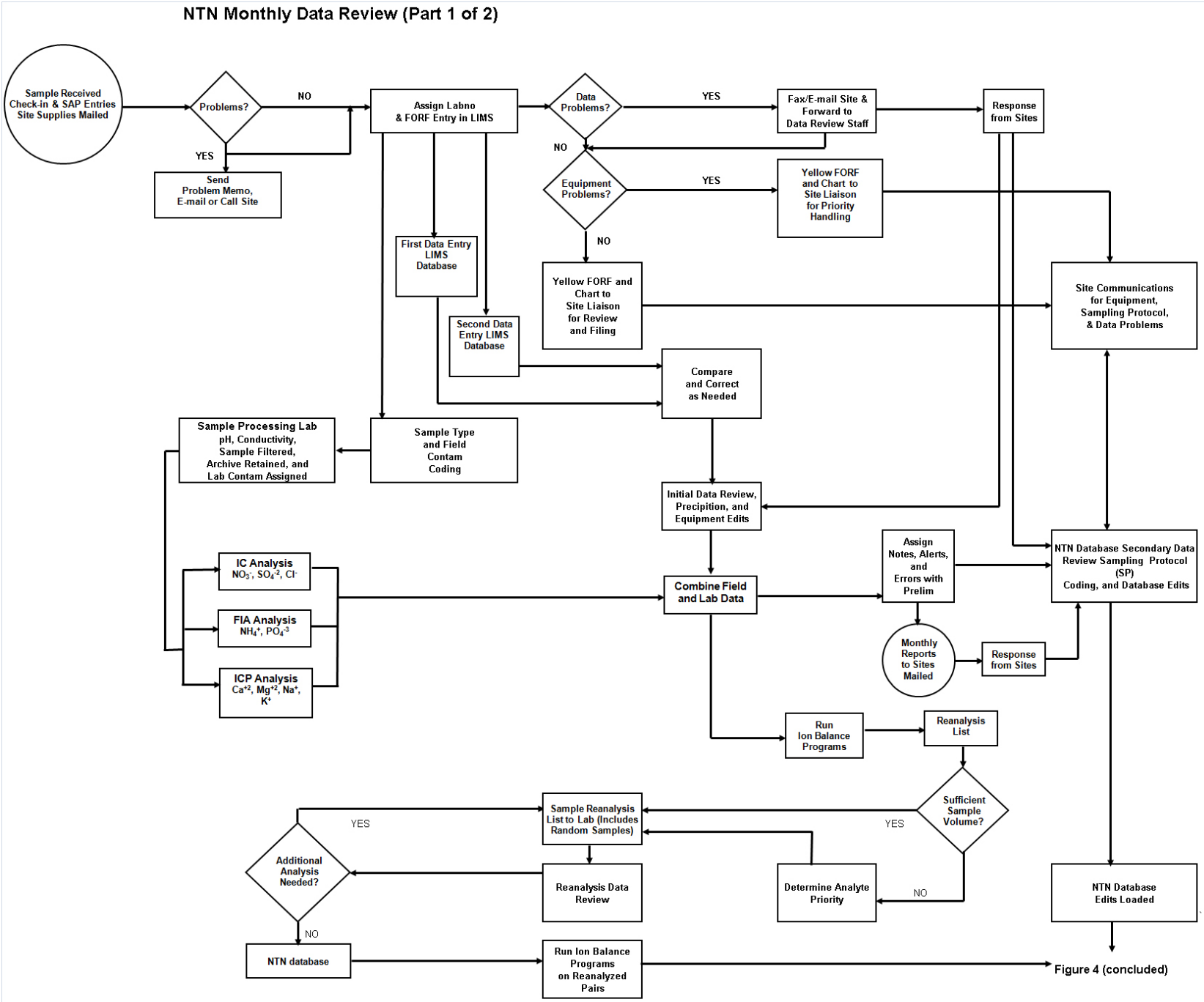

Figure 4. Sample Processing and Data Flowchart, NTN (continued)

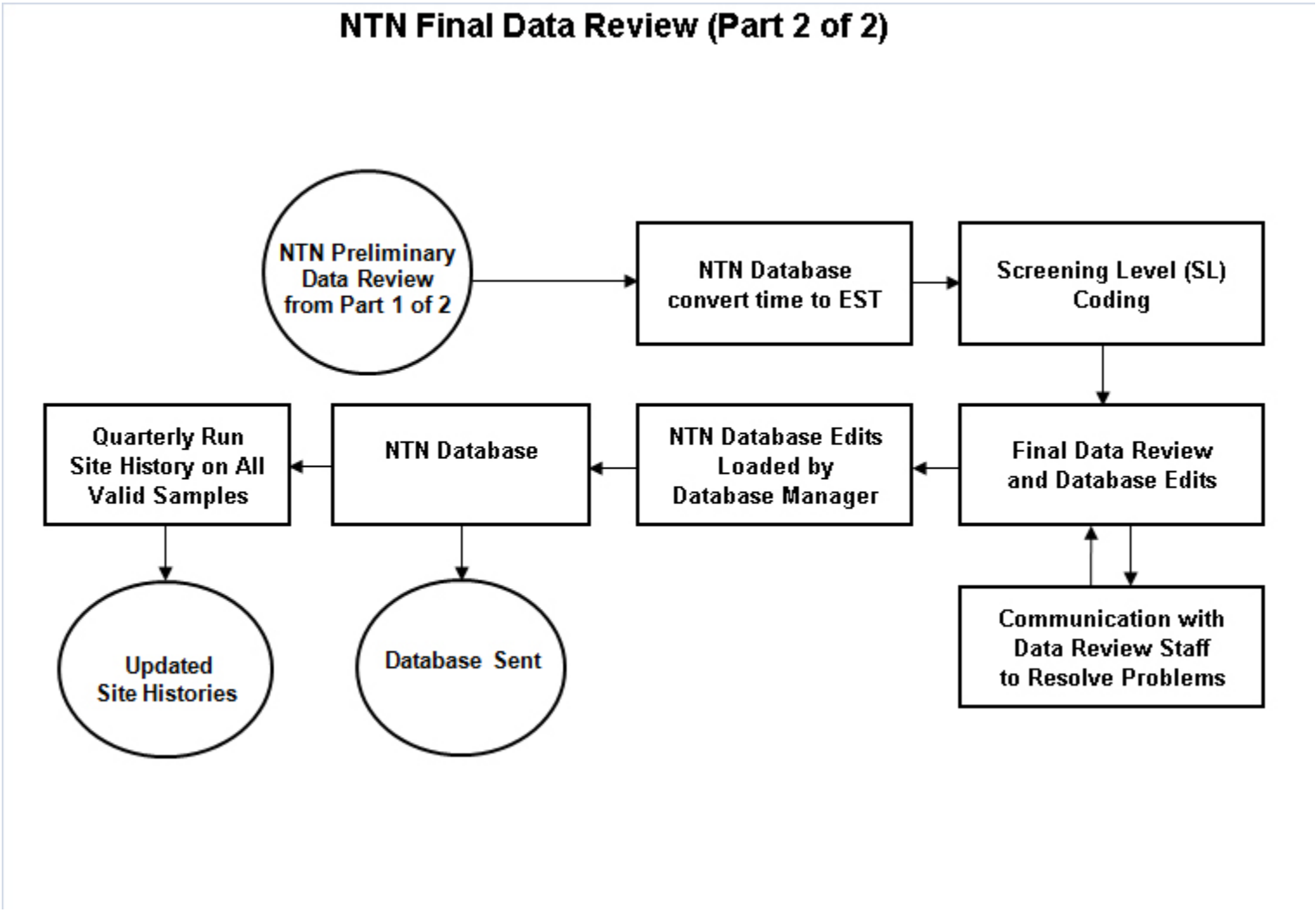

Figure 4 (concluded)

reanalysis values or leaving the original values in the database. For more details concerning the evaluation of the reanalyzed samples, see SOP DA-1031.

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

A series of checks are run from the LIMS which flag samples having unusual collector or raingage function or precipitation data. The data technician responsible for the initial data review checks the FORF and raingage chart for each flagged sample. Edits are based on site communication and re-readings of the raingage chart and FORF, as appropriate.

The NTN Database Manager uses appropriate programs to edit the NTN database and load edits into an edit log table. These programs require a match between what is in the database and site ID, LABNO, 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 DA-0037).

Each month the CAL issues site-specific reports via postal mail or e-mail to each NTN site operator, supervisor, and others upon request. These reports include preliminary results of chemical analyses and FORF information provided by the sites with notes, alerts, and error messages generated by computer programs at the CAL to provide feedback and encourage correction and verification of unusual data. Information facilitating ongoing communication between the sites and the CAL is included with each report (see SOP DA-0037). The CAL Office Administrator mails or e-mails the reports to the sites. Exact procedures may be found in the Office Administrator Training Manual.

The NTN Site Liaison is responsible for secondary review of NTN data to verify accuracy in all field data and preliminary edits and to apply sampling protocol validation codes for each sample. A series of checks, including those utilized in preliminary review and for all other field data (e.g. gaps between samples or sample duration overlaps), are generated by the NTN Database Manager (SOP DA-0037). Edits to the data set are based on faxes, e-mails, phone calls, notes from sites, raingage charts, and FORFs. The NTN Site Liaison also verifies daily precipitation amounts and reconciles those data with daily precipitation types and sampling duration (see SOP SS-1053 for complete details).

The NTN Data Review Specialist conducts the final screening of the data prior to releasing the data set to the PO. The primary goal in the final review is to satisfy final CAL checks of data custody, verification, and screening, and to document data quality and representativeness. Various programs run by the NTN Database Manager facilitate this final review process (see SOP DA-0037). All crucial notes and errors are reviewed to ensure abnormal sampling conditions are documented and sample coding is applied correctly.

After final edits are made, the NTN Database Manager transfers the final data to the PO. A memo is sent to the PO indicating the sample sequence and documenting new sites, discontinued sites, site moves or significant changes, site reopenings, missing samples,

sample gaps greater than three hours, and late samples. The white copies of the corresponding FORFs accompany the memo.

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

All FORF and raingage charts are sent to the PO once the data has been transfered.

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

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

3.0 AIRMoN Description

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

and faxes) to produce a reportable record for each AIRMoN sample. See Figure 5 for the AIRMoN sample processing and data flowchart.

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

When the CAL receives the precipitation sample shipping box, the temperature of the samples is recorded on the FOF (a separate Temp-only bottle is used). The information on the FOF is entered into an RBASE database (see SOP SS-2059 for complete sample receipt details). The same information is reentered into a duplicate database and compared for accuracy (see SOP DA-0037 for complete details). The AIRMoN Database Manager reconciles the differences by checking the disparate entries against FOF data and ensuring the data in the original file matches FOF data.

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

The AIRMoN preliminary data review and reporting uses some of the same programs as NTN data review and reporting but modified for the AIRMoN daily sampling protocols (see SOP SS-2006 for complete details). Between the first and the fifth day of each month, the AIRMoN Database Manager generates preliminary printouts of analytical and field data printouts of the analytical data for the previous month for the AIRMoN Liaison to review. Preliminary printouts are organized by site and contain the sample type, date and time on and off, field chemistry, laboratory chemical concentrations, and the deposition of the analytes in milligrams/square meter. The ion balance and the IPD and CPD are generated from the LIMS and are used to determine samples which need reanalysis. Samples identified in this manner as well as 2% of randomly selected monthly samples are sent to the laboratory for reanalysis. After reviewing preliminary data printouts, the AIRMoN Liaison submits necessary data edits to the AIRMoN Database Manager. Revised preliminary printouts and electronic copies are generated for the AIRMoN Liaison.

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

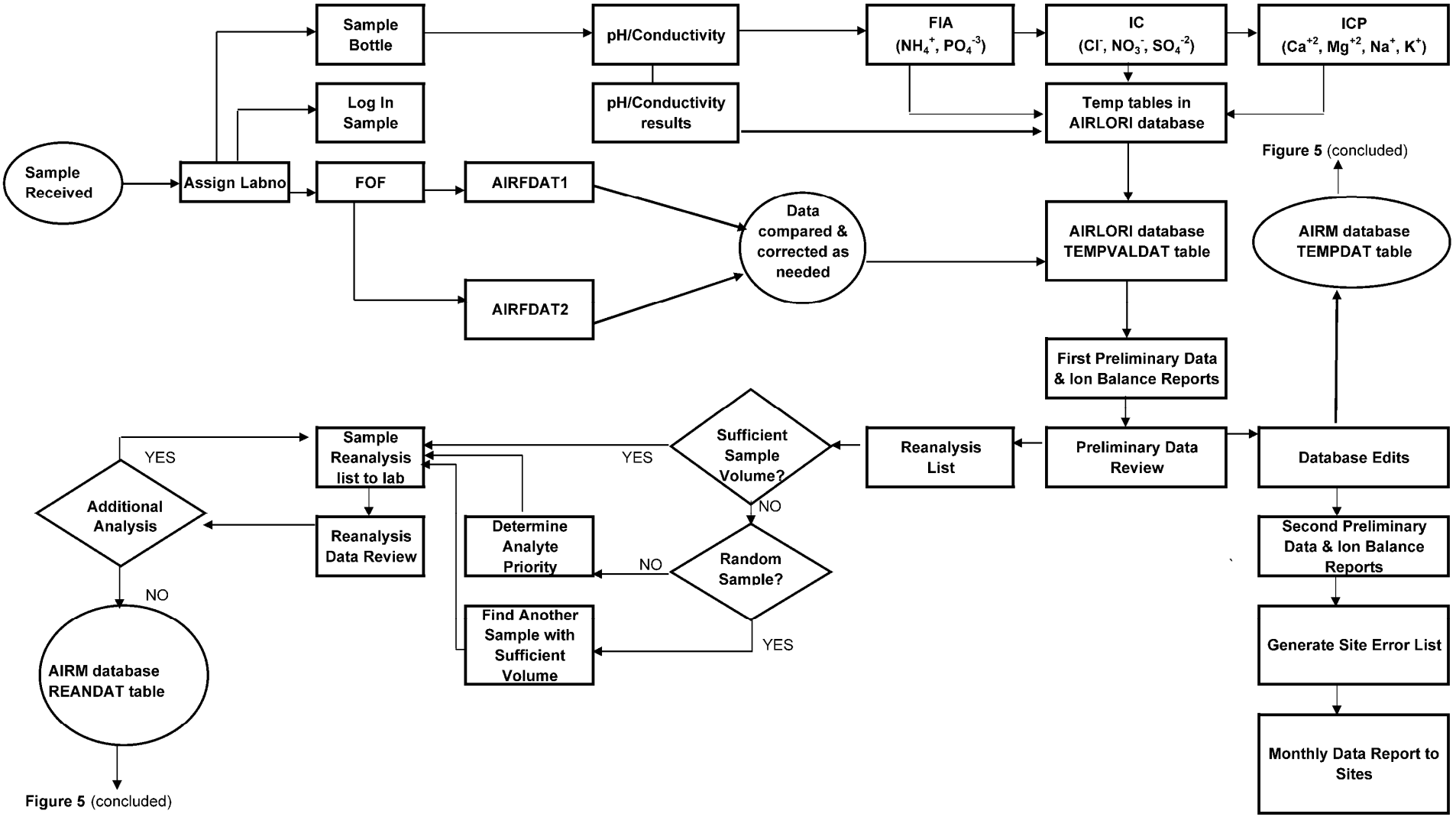

Figure 5. Sample Processing Data Flow Chart, AIRMoN

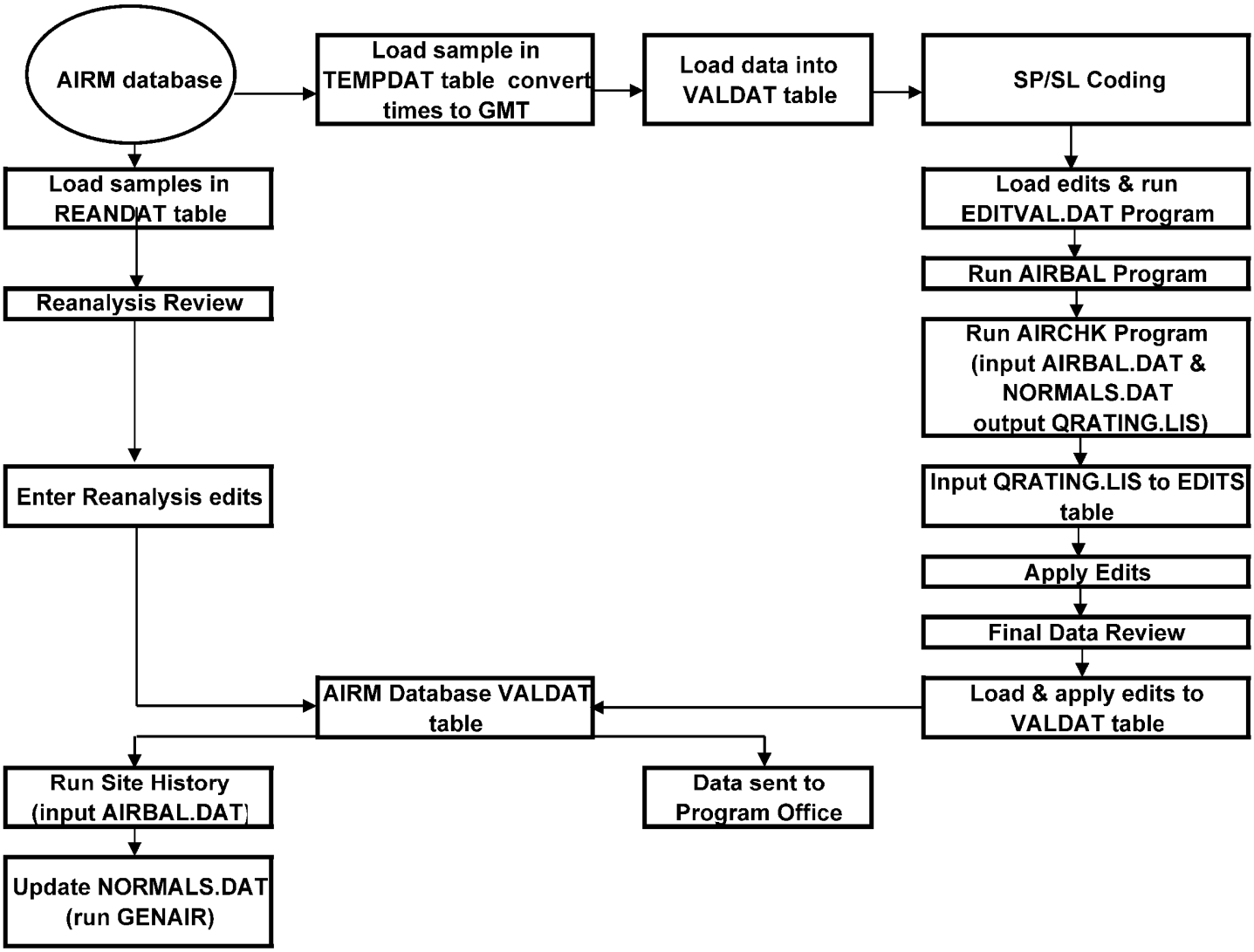

Figure 5 (concluded)

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

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

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

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

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

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

The AIRMoN 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 Liaison's final review of the FOFs (see SOP DATA-58 for complete details).

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

Sample retention policy for AIRMoN differs from that for NTN in that no AIRMoN samples are permanently archived. The AIRMoN samples must be archived for two years after data have been published and then are either disposed of or released to interested parties for additional research.

The AIRMoN Liaison maintains all "AIRCHECK", "PRELIMINARY DATA", "SITE HISTORY", "REANALYSIS", and edit log printouts (see SOP DATA-58 for complete details) for the duration of the project. The AIRMoN Liaison keeps copies of preliminary data letters sent to the sites. For the duration of the project, all electronically submitted preliminary data letters are maintained on the AIRMoN Liaison's computer, which is backed up weekly. For the duration of the project, the AIRMoN Liaison keeps all communications from the Site Operators to the CAL as paper copies or on the computer.

4.0 Data Security

The CAL Database Manager ensures that all computers in regular use have full data backups performed at least once weekly. Backup media are used in rotation, with at least one copy maintained off site at all times. The integrity of backups is evaluated at least once each year to ensure the proper operation of hardware and software.

Paper records are maintained in a secure and environmentally controlled area during their required retention period. Records storage rooms are locked outside of normal business hours. All records must remain at the CAL, unless the Database Manager or CAL Director provide specific permission that they may be taken off site.

Each internally-developed LIMS program and algorithm is tested before regular use by running the old and new systems in parallel, and by regularly auditing data output manually. Each module is tested to ensure expected response under the following data conditions:

- Acceptance of all valid sample data
- Rejection of all invalid sample data
- Rejection or flagging of all data outside of expected ranges
- Reporting of data with expected data notes and flags
- Resistance to inadvertent and unauthorized data changes

The Database Manager is the only staff member authorized to make or facilitate data changes after data are entered or uploaded in LIMS. Individual staff members submit edits to the Database Manager through edits files which are structured as follows:

- Date of change
- Parameter
- Old value
- New value
- Reason for change
- Staff member submitting change
- Date change applied

All edits files are reviewed by the CAL Director before final data submission. All edits files are stored and archived permanently in electronic format.

The ISWS maintains internal network security through network firewalls and campus-wide site licenses for virus protection software. The LIMS is only accessible through direct network wired access or virtual private networking (VPN) from authorized ISWS domain users. The LIMS data integrity is maintained through control of read/write/modification access for individual staff members, and automated logs of data changes. Individual computers for staff are secured through logins and passwords registered to the ISWS domain.

E. Terms and Definitions

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 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.

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.

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.

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 plan (QAP) - 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 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.

technical review – an independent, in-depth analysis and evaluation that may include documents, activities, material, data, or items requiring technical verification or validation for applicability, correctness, adequacy, completeness, and assurance that established requirements are satisfied. It is also used to determine whether quality activities and related results comply with documented procedures such as SOPs and DQOs,

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