QUALITY ASSURANCE PLAN
NADP/NTN DEPOSITION MONITORING

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

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

A contribution to the
Task Group on Deposition Monitoring
Lead Agency: U.S. Geological Survey

The National Atmospheric Deposition Program (NADP) was initiated in 1977 under the leadership of the 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, the first sites of the NADP's precipitation chemistry network were established to provide information about geographical patterns and temporal trends in the deposition of acidic chemicals and nutrients. Initially organized as Regional Project NC-141 by the North Central Region of the SAES, the NADP was endorsed by all four regions in 1982, at which time it became Interregional Project IR-7. A decade later, the SAES reclassified IR-7 as a National Research Support Project, NRSP-3.

In 1982, the federally-supported National Acid Precipitation Assessment Program (NAPAP) was established to provide broadened support for research into the causes and effects of acid deposition. This program includes research, monitoring and assessment activities that emphasize the timely development of a firm scientific basis for decision making. Because of its experience in designing, organizing and operating a national-scale monitoring network, the NADP was asked to assume responsibility for coordinating the operation of the National Trends Network (NTN) of NAPAP. As the NADP and NTN had common siting criteria and operational procedures,and shared a common analytical laboratory, the networks were merged with the designation NADP/NTN. Many of the NTN sites are supported by the U.S. Geological Survey (USGS), which serves as the lead federal agency for deposition monitoring under NAPAP.

Seven federal agencies support NADP/NTN research and monitoring under NAPAP: the USGS, U.S. Department of Agriculture (USDA) Cooperative State Research Service (CSRS) and U.S. Forest Service (USFS), National Park Service (NPS), Bureau of Land Management (BLM), National Oceanic and Atmospheric Administration (NOAA), and the Environmental Protection Agency (EPA). Additional support is provided by various other federal agencies, state agencies, universities, public utilities and industry, as well as the SAES. The current network consists of approximately 200 sites.

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A Cooperative Research Program of the
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and other Federal, State and Private
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(Revised)

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LIST OF ABBREVIATIONS

ADS	Acid Deposition System
APCA	Air Pollution Control Association
AREAL	Atmospheric Research and Exposure Assessment Laboratory
ASCII	American Standard Code for Information Interchange
ASTM	American Society for Testing and Materials
CAL	Central Analytical Laboratory
COED	Coordination Office Equipment Depot
CPD	Conductance Percent Difference
CSRS	Cooperative State Research Service
DBMS	Data Base Management System
DI	Deionized
EST	Eastern Standard Time
FORF	Field Observer Report Form
GMT	Greenwich Mean Time
HDPE	High-Density Polyethylene
IOLM	International Organization for Legal Metrology
IPD	Ion Percent Difference
ISWS	Illinois State Water Survey
MDL	Method Detection Limits
NADP	National Atmospheric Deposition Program
NAPAP	National Acid Precipitation Assessment Program
NREL	Natural Resource Ecology Laboratory
NTN	National Trends Network
NWS	National Weather Service
QA	Quality Assurance
QAP	Quality Assurance Plan
QC	Quality Control
RTI	Research Triangle Institute
SOP	Standard Operating Procedure
UDDC	Unified Deposition Database Committee
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

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Summary of Revisions

The following additions, changes, and corrections to the Quality Assurance Plan are acknowledged:

Revisions		Date
Version: October 22, 1990		
1.	Page 3-9; Figure 3-1, wet side, dry path should have read "add 50 mL DI H_20" not 250 mL.	3 June 1991
2.	Addition of Summary of Revisions page.	3 June 1991

SECTION 1
OVERVIEW OF QUALITY ASSURANCE PROGRAM

1.1 INTRODUCTION

This document is the Quality Assurance Plan (QAP) for all network operations of the National Atmospheric Deposition Program and National Trends Network (NADP/NTN). The Plan describes Quality Assurance (QA) practices for: (a) the selection of network monitoring sites; (b) the operation of field sites; (c) the operation of the Central Analytical Laboratory (CAL); and (d) the documentation, validation, error assessment, archiving, and dissemination of data. Performance criteria for evaluating the effectiveness of the QA and quality control (QC) programs are included, as is a glossary of terms.

1.2 DESCRIPTION OF THE NADP/NTN

1.2.1 Purpose and History

Atmospheric deposition is a major environmental and political concern in North America and Europe. The issues involved are international in scope, transcending political boundaries. Atmospheric concentrations of anthropogenic pollutants have increased substantially since the beginning of this century, and evidence exists that increased pollutant deposition to the earth's surface may be altering biological processes in aquatic and terrestrial ecosystems. Further information is needed regarding the quantity of deposited substances, source-receptor relationships, and the effects of these substances on ecosystems. To obtain this information, scientists have established atmospheric-deposition monitoring stations throughout North America and Europe. Some monitoring stations are site- and study-specific; others are included in long-term, regional, or nationwide monitoring networks and are designed and operated to provide a continuum of quality data. The NADP/NTN is, by far, the largest of these networks. Since the network's inception in 1978, it has produced the largest precipitation chemistry data base in the world.

The National Atmospheric Deposition Program (NADP) was initiated in 1977 by the North Central Region of the State Agricultural Experiment Stations as Project NC-141. This program was given two primary objectives: (1) to establish a network research program to discover and characterize geographical patterns and temporal trends in the chemical climate of North America; and (2) to promote a research program to assess the effects of atmospheric pollutant deposition on crops, forests, soils, animals, surface and groundwaters, and various man-made structures. In 1982, the program was endorsed by all four regions of the State Agricultural Experiment Stations and subsequently became Interregional Project IR-7.

In 1982, the federally supported National Acid Precipitation Assessment Program (NAPAP) was established to provide broadened support for research into the causes and effects of acid deposition. This program includes research, monitoring, and assessment activities that emphasize the timely development of a firm scientific basis for decision making. Because of its experience in designing, organizing, and operating a national-scale monitoring network, the NADP was asked to assume responsibility for coordinating the operation of the National Trends Network (NTN) of NAPAP. Because the NADP and NTN monitoring effort had common criteria for sites and operational procedures and shared a common analytical laboratory, the networks were merged with the designation NADP/NTN. As a result of the NAPAP support, approximately 50 additional sites were added to the NADP/NTN, bringing the total to almost 200 sites.

The NADP/NTN currently measures only wet deposition. Although total deposition (wet and dry) is a critical issue, suitable procedures for routine network measurement of dry deposition are not yet widely available. In addition, costs currently associated with dry deposition measurement techniques may preclude the network-wide use of these techniques. Consequently, the NADP/NTN's policy is to promote the development of new dry deposition measurement techniques and, when feasible, to incorporate those measurements into the network by using suitable devices or techniques that have been thoroughly tested and evaluated. When dry deposition measurements are initiated within the network, dry deposition QA and QC procedures will be incorporated into the Quality Assurance Plan.

1.2.2 Structure and Operation

The NADP/NTN is unique in its structure and mode of operation. It represents hundreds of interested individuals and many state and federal agencies that cooperate to operate atmospheric deposition monitoring sites and to pool data and research efforts under the NADP/NTN umbrella (Table 1-1). The NADP/NTN has become a focal point for atmospheric deposition monitoring and research in the United States.

Table 1-1

Funding Sources For NADP/NTN Monitoring Sites
(MAY 1988)

Funding Agency	Total Sites[a]
U.S. Geological Survey	55
State Agricultural Experiment Stations (non-federal)	26
National Park Service	22
National Oceanic Atmospheric Administration	16
U.S. Forest Service	13
Bureau of Land Management	16
U.S. Environmental Protection Agency	11
Other non-private (state, etc.)	27
Private	13
TOTAL	199

[a]Based on contracts for funding chemicals analysis. In many cases, a second agency or organization provides operational support for the site.

Several groups have unique roles in producing NADP/NTN data. According to network protocols, sites use standardized instrumentation and procedures to make field measurements and to collect weekly wet deposition samples. The samples are sent to the Central Analytical Laboratory (CAL) at the Illinois State Water Survey (ISWS), where all samples are analyzed according to documented procedures. The data obtained from the sites and from the CAL are combined into a data base and distributed to all sites and to the public upon request. Annual summaries and reports are also made available through the Coordination Office at Colorado State University and through the U.S. Environmental Protection Agency's (USEPA) Acid Deposition System (ADS).

1.3 ORGANIZATION AND RESPONSIBILITIES

1.3.1 Organization of NADP/NTN

The quality assurance program is a cooperative effort of the National Atmospheric Deposition Program, the NAPAP Task Group on Deposition Monitoring (Task Group IV), the

U.S. Geological Survey (USGS) and the USEPA. In its general structure, the organization of the NADP/NTN follows the guidelines established for interregional research projects by the Cooperative State Research Service (USDA, 1977). With the formation of the NADP/NTN network in 1983, the federal agencies agreed to work within the existing NADP organizational framework. The major components of the organization are diagrammed in Figure 1-1.

1.3.1.1 Technical Committee

The Technical Committee operates as a "committee of the whole" to set policy and make decisions concerning the technical and scientific aspects of the program. Typically, the issues it considers are introduced by the subcommittees (see section 1.3.1.6) as recommendations. Before coming to a general vote, issues raised from the floor of the Technical Committee are often referred to a subcommittee or to an *ad hoc* working group for further study. Decisions of the Technical Committee are determined by a simple majority vote of attending program participants. Membership follows U.S. Department of Agriculture - Cooperative State Research Service (CSRS) Cooperative Regional Project rules (USDA, 1977). The committee meets annually.

1.3.1.2 Executive Committee

The Executive Committee conducts the business of the Technical Committee between Technical Committee meetings and also performs other tasks assigned by the Technical Committee. Decisions concerning the administrative and budgetary aspects of the program are made by this committee. The voting membership of the Executive Committee consists of the program chairman, vice chairman, secretary, past chairman, the chairman of each of the three subcommittees, and the chairman of the Quality Assurance Steering Committee. Sitting on this committee as advisors are the State Agricultural Experiment Stations' (SAES) regional administrative advisors, the CSRS representative, the USGS representative, the director of the CAL, the program coordinator, and the NAPAP representative.

The Executive Committee meets semiannually. Decisions are determined by a simple majority vote of attending members.

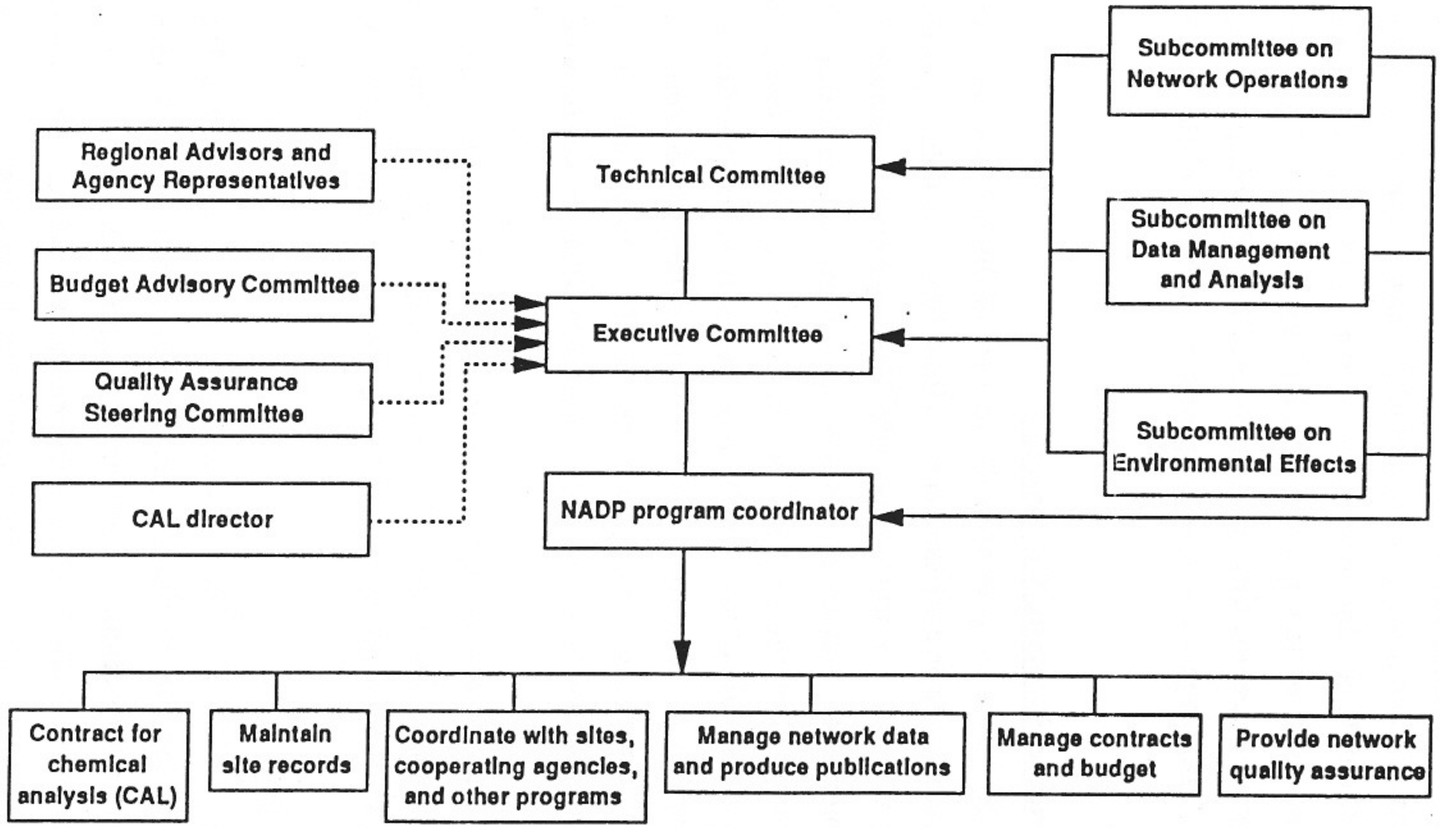

Figure 1-1. Organization of the National Atmospheric Deposition Program

1.3.1.3 Budget Advisory Committee

The Budget Advisory Committee, comprised of the past and present chairmen of the NADP/NTN Technical Committee, the chairman of the SAES Regional Administrative Advisors, and representatives of the primary funding agencies for the network, meets annually to review program expenditures and to plan for future funding. The committee is co-chaired by the NAPAP representative and the program chairman of the NADP Technical Committee.

1.3.1.4 Quality Assurance Steering Committee

Although many QA issues are primarily the concern of the Subcommittee on Network Operations, other subcommittees do consider issues related to network data quality. Because there is overlap among the subcommittee responsibilities regarding QA issues, the Quality Assurance Steering Committee was established to coordinate and arbitrate QA matters referred to it by the various subcommittees and to oversee the implementation of the Quality Assurance Plan. The membership of the Quality Assurance Steering Committee consists of the chairman, the chairman or delegate of each subcommittee, the coordinator, the CAL director, the network QA manager, representatives of the USGS and the USEPA, and additional participants appointed by the Quality Assurance Steering Committee chairman.

The Quality Assurance Steering Committee meets at least once each year. Additional meetings are held as needed. Decisions are made by simple majority vote of attending members. The charges and responsibilities of this committee are described in section 1.3.2.

1.3.1.5 Coordination Office

The staff of the NADP/NTN Coordination Office at Colorado State University is responsible for administering the monitoring program on a daily basis. General areas of responsibility are shown on the organizational chart in Figure 1-2. Primary responsibilities of the coordinator include budget and funds management; data management; the production of annual data summaries and other network reports; site documentation; contracting with the CAL for analytical services and with the sites for analytical costs; coordinating with cooperating agencies and other programs; and performing other activities that enable the

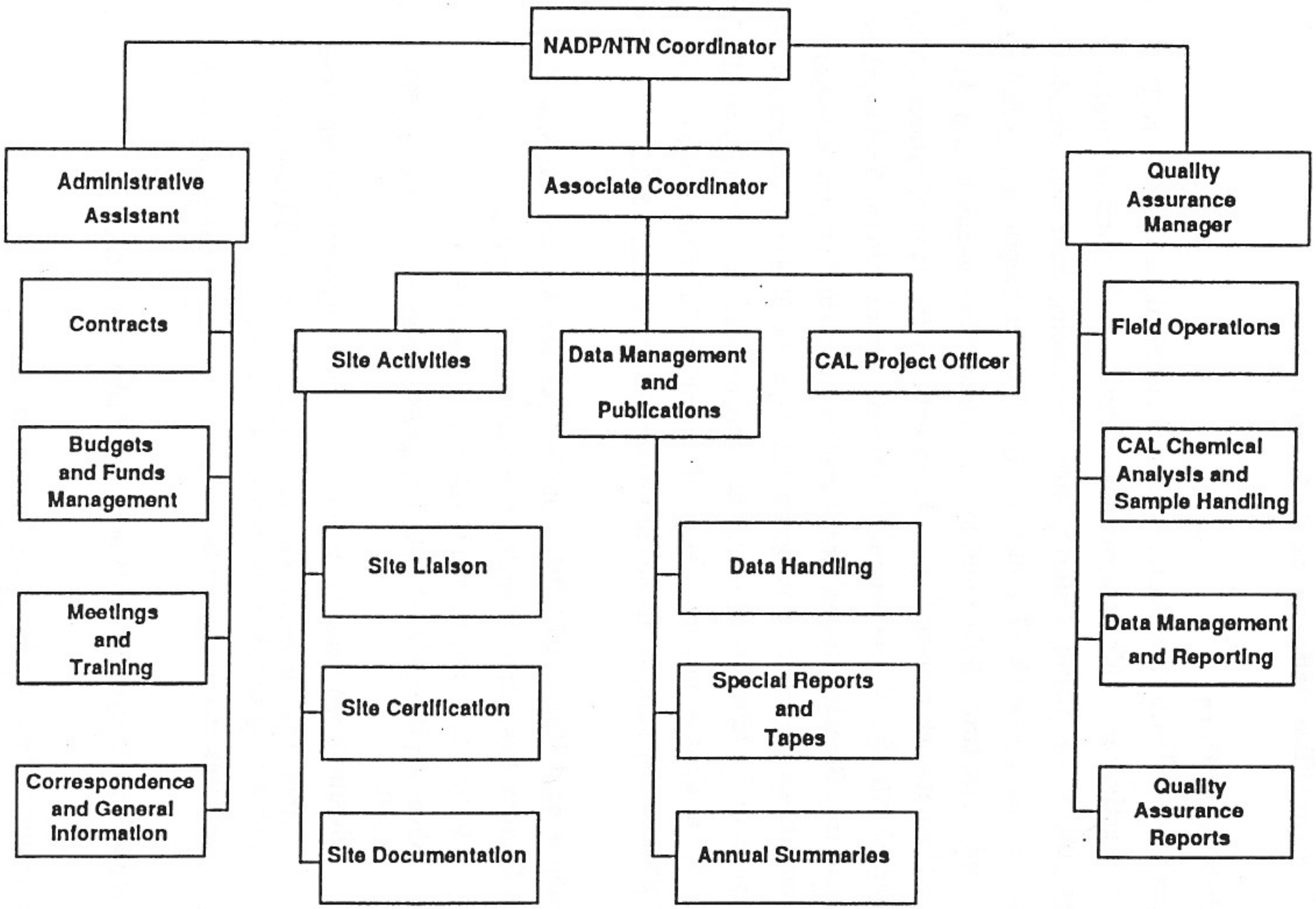

Figure 1-2. Organization of NADP/NTN Coordination Office

network to function smoothly. The NADP/NTN quality assurance manager is the member of the Coordination Office staff responsible for network QA.

1.3.1.6 Subcommittees

Three permanent subcommittees provide technical guidance for NADP/NTN monitoring and research activities. Matters considered by the subcommittees relate to: (a) network operations, including siting criteria, site operations, methods development, and QA (Subcommittee on Network Operations); (b) data management, including data coding, analysis, and reporting (Subcommittee on Data Management and Analysis); and (c) interfacing the network monitoring program with environmental effects (Subcommittee on Environmental Effects). These committees provide input into the Technical, Executive, and Quality Assurance Steering Committees through reports and recommendations. Membership in these committees is open to all program participants. The subcommittees convene at least once each year, and additional meetings are held as needed. Decisions in all subcommittees are made by a simple majority vote of members in attendance. The charges and responsibilities of the subcommittees are described in section 1.3.3.

1.3.2 Charges and Responsibilities of the Quality Assurance Steering Committee

The Quality Assurance Steering Committee is charged to:

1. Review and update the Quality Assurance Plan.
2. Oversee the network QA manager's implementation of the Quality Assurance Plan.
3. Evaluate QA documents prepared by the network QA manager.
4. Direct the development and updating of a bibliography of publications pertaining to the network's QA activities.
5. Oversee the implementation and execution of the Remedial Action Plan.

1.3.3 Charges and Responsibilities of the Subcommittees

1.3.3.1 Subcommittee on Network Operations

The Subcommittee on Network Operations is charged to:

1. Recommend and evaluate siting criteria, instrumentation, procedures, methods, and technologies proposed for use by the network.
2. Review and evaluate field measurement procedures to assure that proper protocol is followed and make recommendations as appropriate.
3. Evaluate and determine the acceptability of changes made or proposed by the CAL concerning analytical methods, laboratory procedures, and QC.
4. Assure that the appropriate analytical procedures are used and that appropriate QC and QA protocols are followed by periodic reviews/audits of the CAL analytical section and the external quality assurance program.
5. Assure that the analytical data that are generated for the network meet the needs of the program and are accompanied by complete QA documentation, as outlined in the Quality Assurance Plan; when the needs of the program change, this subcommittee reviews and recommends changes in the Quality Assurance Plan on matters of network operations.
6. Review and approve the instruction manuals for selecting and operating sites.
7. Provide reports to the Technical Committee and the Executive Committee as appropriate; copies of these reports are sent to the network QA manager and the agency representatives of the external audit programs.
8. Provide technical support to the Quality Assurance Steering Committee.

1.3.3.2 Subcommittee on Data Management and Analysis

The Subcommittee on Data Management and Analysis is charged to:

1. Recommend and review procedures for recording measurements and observations reported by field site operators, the CAL, the Coordination Office, and by external auditing agencies. This includes the review and approval of the design of the Field Observer Report Form and the precipitation gage chart.
2. Review, evaluate, and make recommendations on the instruction manual for site operation or proposed changes in this manual, especially where methods or criteria for recording or reporting data are described.
3. Review and recommend proposed changes in data management procedures to improve accuracy or efficiency in current practices and to meet new or modified objectives.
4. Review and approve all standard operating procedures (SOPs) relating to data management and reporting including all proposed changes to these documents. This includes all data screening and coding procedures used by sites, the CAL, the Coordination Office; and all criteria for data reporting.
5. Review and approve the format of data reports and summaries from the CAL and the Coordination Office and recommend changes consistent with reporting objectives; evaluate and approve the criteria for including site data in these reports and summaries.

6. Assure that appropriate data management procedures are used and that appropriate QA and QC protocols are followed by participating in the technical reviews and audits of the CAL and Coordination Office data management operations.

7. Assure that the network data meet the needs of the program and are accompanied by complete QA documentation, as outlined in the Quality Assurance Plan; when the needs of the program change, this subcommittee reviews and recommends changes in the Quality Assurance Plan on matters of network data management operations.

8. Provide reports to the Technical Committee and the Executive Committee as appropriate; copies of these reports are sent to the network QA manager and the agency representatives of the external audit programs.

9. Provide technical support to the Quality Assurance Steering Committee.

1.3.3.3 Subcommittee on Environmental Effects

The Subcommittee on Environmental Effects is charged to:

1. Advise the NADP on the atmospheric deposition data needs of effects research scientists.

2. Make recommendations to the CSRS on priorities for research funding.

3. Promote communication and cooperation among effects researchers.

1.4 OBJECTIVES AND GOALS

1.4.1 Scope

Because the concentrations of dissolved materials in precipitation are generally quite low (< 20 mg/L dissolved solids), the chemical characteristics of precipitation samples are potentially subject to appreciable error. These errors can result from: sample contamination; chemical, physical, or biological changes in the sample; or variations in collection or analytical procedures. Stringent QA and QC procedures are essential for obtaining unbiased, precise, and representative atmospheric deposition measurements and for maintaining the integrity of the sample during collection, handling, and analysis. Equally stringent procedures must be applied to data management to assure that the accuracy of the data is maintained.

QA is stressed in all aspects of the network's operation. Sites are expected to meet minimum siting criteria and use approved instruments and procedures to participate in the network. The CAL operates under a well-defined QA program with stringent QC criteria. QA continues for processing, coding, and reporting data to the Coordination Office. The QA plan, however, is not a static set of rules. QA procedures are modified to accommodate growth and other changes in the network and in response to the experience accumulated from past practices. Accordingly, the Quality Assurance Plan is reviewed annually by the QA Steering Committee and revised as needed.

1.4.2 Quality Assurance Policy

Policy is formulated by the Quality Assurance Steering Committee in conjunction with the subcommittees on network operations, data management and analysis, and effects research. Policies are approved by the Technical Committee. The overall goal of these policies is to ensure that all data collected by or for the program are of such high quality that they offer maximum credibility. QA programs, therefore, are aimed toward providing representative data of documented bias, precision, and completeness to assist data users in evaluating the appropriateness of the data for a particular application. Specifically, it is NADP/NTN policy to accomplish the following:

1. Provide quality assessments of network operations to assist network management and cooperating agencies in improving network monitoring strategies.
2. Provide estimates of completeness, precision, bias and representativeness for all spatial and temporal data values reported by the network.
3. Provide complete and concise records of network policies, procedures and quality assessments.
4. Associate network quality assurance documentation permanently with the monitoring network's data.

1.4.3 Quality Control Programs

The major components of any QAP are sound QC programs. The results of such programs assure the data user that the reported values and associated error terms are accurate. Quality control is the use of specified methods and procedures that meet prescribed performance standards in routine field, laboratory, and data management operations. In the NADP/NTN monitoring program, quality control is applied to all aspects of monitoring, measuring, and reporting of atmospheric deposition variables. Performance standards for bias and precision are established for each measurement and operation; these are based on knowledge of the measurement system employed. Validation procedures include using known standards, accepted calibration procedures, replicate samples, spikes, blanks, split samples, blind samples, reagent checks, system audits, ion balance, data checks, and verifying data processing procedures when appropriate. The quality control program consists of three parts that correspond to the field operations, the laboratory operations, and the data management operations of the network. Quality control standards are detailed in the sections of this plan pertaining to these operations.

1.4.4 External Quality Assurance Programs

Sites are visited once every 2-3 years to identify technical problems of siting, equipment and operational practices. The visits document the local source emissions in the vicinity of the site, near-by land-use and the site's adherence to network siting criteria. The condition of equipment, the performance of the site personnel, and the results of various QA tests are also documented.

Field measurements of pH and conductance are monitored through a second program in which site operators analyze simulated precipitation samples on a semiannual basis. A third program monitors precision and bias of network chemical measurements through a two-phase blind audit sample program. Audit samples are sent to sites randomly selected from each of the four regions in the network. At the site a portion of the sample is poured into a bucket by the site operator and is treated as a true precipitation sample through all stages of the network's sample handling and analytical procedures. The remainder is sent directly to the CAL in the original bottle for separate analysis. A fourth program provides an assessment of the comparability of the network's laboratory data through the CAL's participation in several interlaboratory comparison programs. A fifth program estimates within-site and overall network precision through the operation of collocated samplers for one-year periods at selected sites. These programs are described in greater detail in Sections 2 and 3.

1.5 REMEDIAL ACTION PLAN

1.5.1 Description

The Remedial Action Plan describes the sequence of actions taken to resolve problems of noncompliance with NADP/NTN procedures, protocols, and criteria. The plan applies to violations of sampling protocols and siting criteria by established sites, unacceptable laboratory and data management procedures, and a site's failure to participate in QA programs. A flow chart of the plan is shown in Figure 1-3.

1.5.2 Sequence of Actions

Reports of noncompliance with program procedures, criteria, and protocols are initially referred to the QA manager. Possible sources of such reports are the CAL, external quality assurance programs, the Coordination Office, the NADP subcommittees, and site operators and supervisors. The QA manager determines the cause of the noncompliance and, if possible, rectifies the situation by assisting the noncomplying party in solving the problem that led to violation. Problems addressed in this manner are likely to be minor, such as those involving miscommunication between program participants. The problems and their solutions are summarized by the QA manager in semiannual reports to the Quality Assurance Steering Committee.

Problems not resolved by the QA manager are referred to the Coordinator. The Coordinator and his staff work closely with the noncomplying party in an effort to achieve compliance. Such problems are reported to the Quality Assurance Steering Committee on a semiannual basis. In cases where compliance with program procedures, criteria or protocols cannot be achieved and where a precedent has been established by the QASC for an exemption, the Coordination Office may grant one. The Coordination Office and the QA manager's actions are subject to review by the Quality Assurance Steering Committee, which reports them to the Technical Committee in an annual summary. Moreover, the actions are documented in the site files or laboratory files (Figure 1-3, Path A). The resolution of problems involving site operations are reported to the site supervisors and sponsors by the Coordination Office.

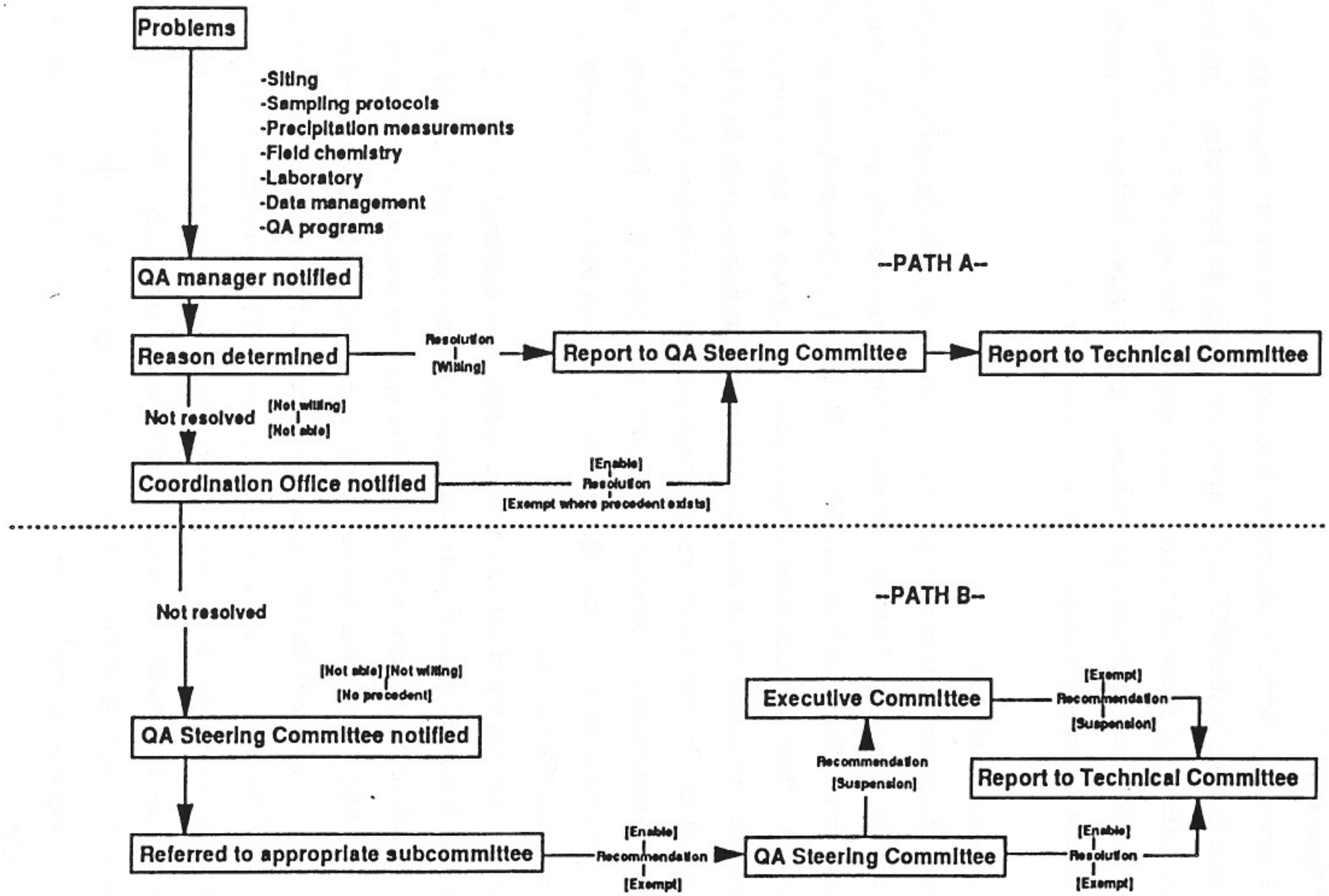

Figure 1-3. Flow Chart of the NADP/NTN Remedial Action Plan

In the event that a problem cannot be resolved by assisting the noncomplying party in conforming to the procedures, criteria, or protocols--or in the event that a precedent for action on the part of the Coordination Office is lacking--the problem is referred to the Quality Assurance Steering Committee (Figure 1-3, Path B). The committee then refers it to the appropriate subcommittee(s). The Coordination Office provides as much information as possible to aid the subcommittee(s) in analyzing the problem and may also recommend a course of action. The subcommittee(s) reviews the problem and recommends a course of action to the Quality Assurance Steering Committee, which has the responsibility to evaluate the recommendations submitted by the subcommittee(s) and to decide on a course of action.

A decision to suspend a participant from the program requires the approval of the Executive Committee. All other remedial actions are determined by the majority vote of the Quality Assurance Steering Committee. Problems requiring remedial action and their resolution are reported to the Technical Committee on an annual basis. Remedial actions by the Quality Assurance Steering Committee and the Executive Committee are documented in the site and laboratory files and reported to the site supervisor or CAL director.

1.6 REPORTING AND DOCUMENTATION

Quality assurance reports, assessments and SOPs, originating from a variety of sources are provided to the Quality Assurance Manager and are maintained in the Coordination Office. These documents include but are not limited to the following:

1. The Quality Assurance Plan
2. The Site Selection and Installation Manual
3. The Instruction Manual for Site Operations
4. The work plans for external quality assurance programs
5. Analytical methods and data management procedures
6. The Central Analytical Laboratory's Quality Assurance Plan

SECTION 2
FIELD OPERATIONS

2.1 DESCRIPTION

This section presents the plan for defining and controlling the quality of sample collection and measurement activities at the NADP/NTN precipitation collection sites. Included in these activities are the selection and installation of monitoring locations; the collection of both wet and dry samples of atmospheric deposition; the measurement of pH, specific conductance and rainfall amount in collected samples; the maintenance of sample collection and measurement instrumentation; the quality control and quality coding of field measurements and observations; and the instruction of site personnel in the standardized procedures used by the monitoring program.

Candidate sites are evaluated by the Coordination Office for their suitability for meeting the long-term spatial and temporal objectives of the program. This evaluation is based upon criteria detailed in Bigelow (1984) and in the NTN design document (Robertson and Wilson, 1985). Each network site is located and installed by the site's sponsor or a network representative following these siting criteria.

The network measures wet deposition at each site and dry deposition (dry bucket) at a subset of sites using an Aerochem Metrics wet/dry collector (Bigelow and Dossett, 1988). Precipitation samples accumulate in the wet-side bucket of the collector for one week and are removed each Tuesday at approximately 9 a.m. local time. Dry-side buckets are also removed on Tuesdays but on an eight week schedule.

At the field site, all samples containing water are weighed. For wet-side samples with sufficient volume, an aliquot is withdrawn and analyzed for pH and specific conductance. Precipitation amounts are also measured independently using a Belfort 5-780 Universal Precipitation Gage ("rain gage") which is equipped with an event marker to record the opening and closing cycles of the wet/dry collector. Finally, when all required measurements have been made and all necessary observations have been recorded, samples are shipped to the Central Analytical Laboratory (CAL) in their original container. Each sample is accompanied by a completed standardized reporting form, the Field Observer Report Form (FORF) and by a precipitation gage chart.

Equipment is maintained and checked according to standard procedures specified in a site operation instruction manual (Bigelow and Dossett, 1988). Replacement parts for sample collection equipment and pH electrodes are furnished to sites on an as needed basis. Troubleshooting of all aspects of site operations is available through two site liaisons; one at the CAL and one at the Coordination Office. A training course and video are also available for instructing site personnel in the procedures used by the network to collect, measure and document deposition samples.

2.2 ORGANIZATION AND RESPONSIBILITIES

Field site operation is the responsibility of the site's sponsor. The sponsor provides or designates a site supervisor and site operator. The operator or supervisor may further designate an observer to assist the operator in the weekly operation of the site. In some instances when the site's supervisor is not also the site operator's work supervisor, site operation becomes the joint responsibility of the sponsor and the operator's employer. Technical support for site personnel is provided by the site liaisons at both the CAL and the Coordination Office.

2.2.1 Site Sponsor

The site sponsor provides or makes arrangements for the financial resources that are necessary to pay for the operation of the monitoring site and provides or designates a site supervisor and site operator. The financing of the site operation includes not only the cost of chemical analysis but also the cost involved in furnishing manpower, sampling equipment, site security and site maintenance. Site maintenance includes both the repair and replacement of sampling and site laboratory equipment as well as the maintenance of required on-site sampling conditions (weed control, tree cutting, road access, etc.). Oftentimes the cost of operating a monitoring site is shared among cooperating agencies.

2.2.2 Site Supervisor

Site supervisors are responsible for overseeing site operations and for ensuring that NADP/NTN sampling and siting protocols are followed. Site supervisors typically review the weekly data produced at the site, assist the site operator in troubleshooting operational

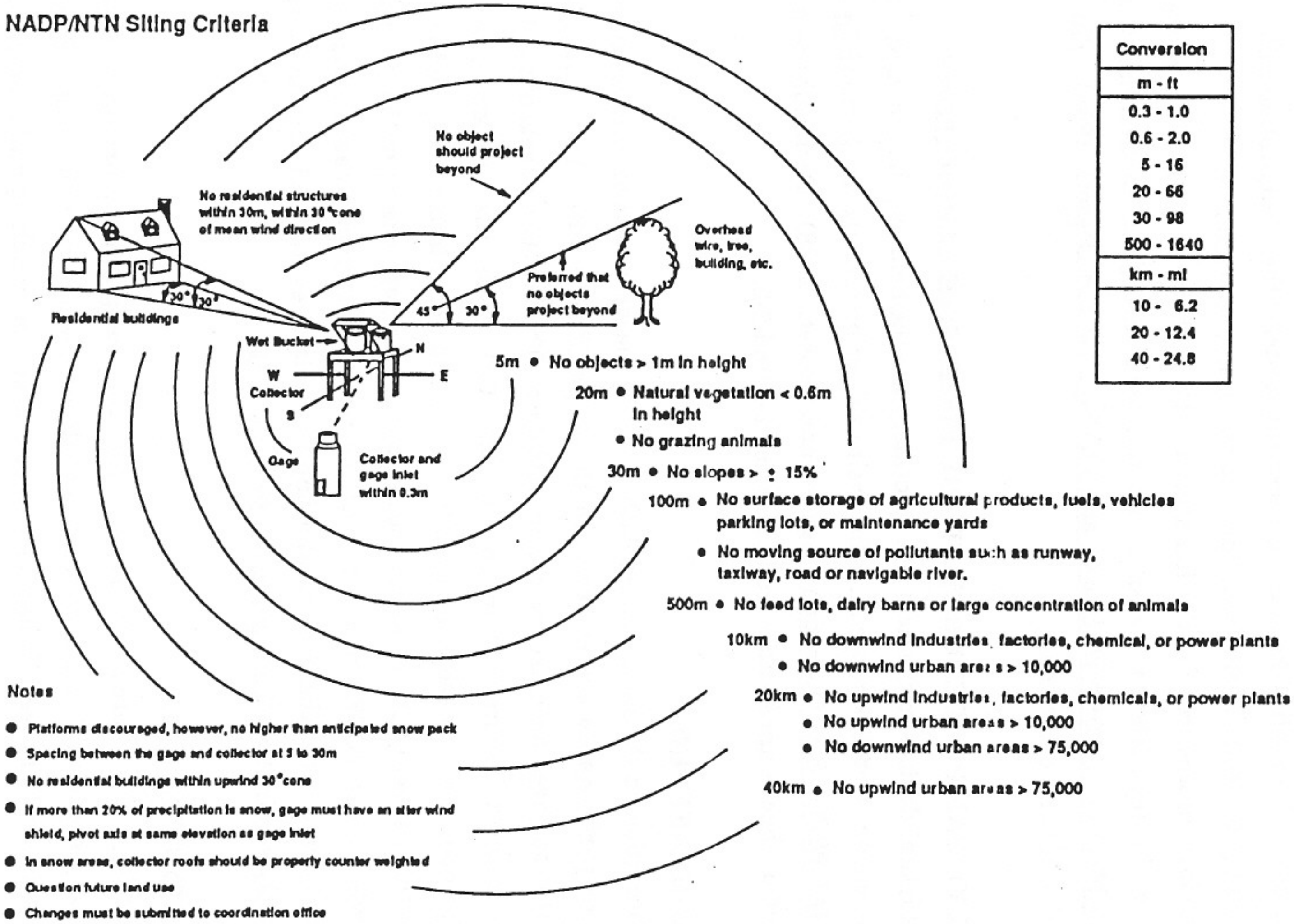

Figure 2-1. NADP/NTN Siting Criteria.

2.4 SAMPLE COLLECTION

The network specifies the manufacturer and model of the precipitation collector, event recorder, rain gage, and pH electrode that are to be used at each site.

Standard procedures for the handling of the buckets as well as for checking, and maintaining the precipitation collector and rain gage are given in Sections 2 and 3 of Instruction Manual: NADP/NTN Site Operation (Bigelow and Dossett, 1988). This manual is provided to all site operators.

2.5 ANALYTICAL PROCEDURES AT THE FIELD SITE LABORATORY

Analytical devices in the field site laboratory are the balance, the conductivity meter, and the pH meter. Detailed procedures for their calibration and use are given in Instruction Manual: NADP/NTN Site Operation (Bigelow and Dossett, 1988). Performance goals and quality control checks are summarized in Tables 2-1 and 2-2.

2.6 RECORD KEEPING

Information on the sample, the weather during the week, activities near the collector, and collector performance are recorded on the FORF (Figure 2-2). This is a carbonless, triplicate, standardized form used to record field data. The first two sheets of the FORF and the rain gage chart (Figure 2-3) are sent to the CAL with the weekly precipitation sample. The operator also keeps a journal to record additional information and is expected to keep the third sheet of the FORF and copies of the rain gage charts on file for reference. Entries made on the FORF are checked at the time of entry for reasonableness by the operator, and again when the site operator and supervisor review the information returned in the monthly preliminary data printouts from the CAL.

2.7 QUALITY CONTROL

Several QC checks are made to ensure that the precipitation collector, rain gage and field laboratory equipment are operating correctly and within specifications. Briefly, the collector is maintained by weekly diagnostic checks of sensor switching and heater operation, motor unit driving and switching functions, and the foam lid pad seal and condition. Field laboratory equipment is also routinely checked and calibrated. Field equipment and laboratory checks are summarized in Table 2-2. Detailed explanations of the field site QC procedures, reasons for their use, and results of checks are available in Stensland et al. (1983), and in Bigelow (1986).

Table 2-2

Quality Control Checks and Corrective Actions at Collection Sites

Device checked and check	Frequency	Expected response	Probable cause of problem	Corrective action
<u>Precipitation collector</u>				
Lid liner and cleanliness (Visual inspection)	Every 8 weeks (every week without precipitation)	Good seal evident, dustfree, no cracks or mildew; low-dynamic blank analyses	Lid liner worn out; incorrectly mounted	Replace lid liner
Wet- and dry-bucket contents (visual inspection)	Weekly	Uncontaminated wet-side sample. No water in dry-side bucket	Collector malfunctioning	Replace motor box and/or sensor
Sensor activates (add water; observe rain gage event marker trace; notice motion of lid)	Weekly	Event marker responds; collector lid moves	Motor box bad; battery dead; bad connection; shorted out; weak battery; incorrect adjustment; shorted out	Check power; correct power; replace motor box
Sensor heats (add water; touch with finger, after 5 min; observe rain gage event marker trace)	Weekly	Warm to touch	Motor box or sensor malfunction	Replace motor box and/or sensor

Table 2-2 (Cont'd)

Device checked and check	Frequency	Expected response	Probable cause of problem	Corrective action
Rain Gage				
Event marker responds (activate collector sensor with water; observe response)	Weekly	Event marker displaces upward and returns to baseline after sensor dries	Broken wire; bad solenoid; no ink	Replace wire and/or solenoid. Ink pen.
Accuracy or response (add sand-filled bottles and observe)	Periodically	Accurate to ±0.1 in of known weight	Incorrect zero offset, calibration, etc.	Calibrate. Clean.
Crossover accuracy (observe)	Periodically	Crossover occurs at 6 ± 0.1 in	Maladjusted crossover screw	Adjust crossover.
Pen mechanism (look for sharp, unexpected pen movements)	Weekly	Smooth and continuous movement of the pen	Corrosion on linkages	Clean corrosion.
Clock mechanism (compare pen mark to wrist watch)	Weekly	Accurate date and hour correct ±2h	Clock motor dirty or worn; weak batteries	Replace clock, replace batteries.
Conductivity Meter and Cell				
Accuracy of response (electrode test solution)	Weekly	Accurate within ±4 µS/cm	Dirty cell, broken cell	Replace cell, clean cell
pH Meter and Electrode				
Accuracy of response (electrode test solution)	Weekly	Accurate to ± 0.1 pH unit at known value of 4.30	Bad electrode or rinse water	Replace electrode; get better water
Balance, mass				
Response to weights of known mass	Periodically	Accurate to within ±1 g	Balance incorrectly set up; zero adjusted incorrectly; worn knife-edge	Check balance; replace knife-edge

NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

NADP/NTN FIELD OBSERVER REPORT FORM

Send Completed Form With Each Bucket

CAL/NREL Use Only

N

BAG LEAK

SP SL

1. STATION Name ______ ID

2. OBSERVER ______ Signature Initials

3. SAMPLE BUCKET *Check One* Wet-Side Dry-Side

4. BUCKET ON Date MO DAY YR Time 0000-2400

BUCKET OFF Date MO DAY YR Time 0000-2400

5. SITE OPERATIONS *Check Yes or No for all Wet-Side samples.*

YES	NO	
		1. The sensor heater and motor box operated properly and the event recorder indicates the collector lid closed promptly at the end of each precipitation event.
		2. Rain gage appears to have operated properly during the week.
		3. Collector opened and closed at least once during the week, other than for testing.

6. SAMPLE CONDITION

Check Yes or No for all samples containing precipitation

YES	NO	
		1. Bird Droppings
		2. Cloudy or Discolored
		3 Unusual amounts of soot or dirt for this site

7. SAMPLE WEIGHT

For all buckets containing precipitation

Bucket + Lid + Sample

− Bucket + Lid

= Sample Weight in grams

8. PRECIPITATION RECORD *For Wet-Side Samples Only*

R - Rain Only
S - Snow Only
M - Mixture
U - Unknown
Z - Zero
T - Trace
MM - Missing

Bucket On → To → Bucket Off

	TUES	WED	THUR	FRI	SAT	SUN	MON	TUES
Type Circle one	R S M U	R S M U	R S M U	R S M U	R S M U	R S M U	R S M U	R S M U
Inches or circle one	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM	Z T MM

Total sampling period precipitation from rain gage ____ Inches

Total precipitation from sampler = Sample Weight × 0.00058 Inches/gram ____ Inches

9. SAMPLE CHEMISTRY

Only for Wet-Side buckets with a Sample Weight of more than 70 grams.

MO DAY YR

Aliquot Removed in mls

Conductance in μS/cm

7 5 . 0 Standard Certified + Standard Measured − Distilled Water = Correction Factor

Correction Factor × Check Sample Measured = Check Sample Corrected

Correction Factor × Precipitation Sample Measured = Precipitation Sample Corrected

pH

Precipitation Sample

pH Check Sample

10. SUPPLIES

Circle if needed
pH 4 Buffer
pH 7 Buffer
Check Sample
75 μS/cm Standard
Field Forms
Vials
pH electrode
Rain gage chart
Rain gage ink

11. REMARKS *For example: Insect contamination, contamination by operator, equipment malfunction, harvesting in area, etc.*

REVISED 4/87

Figure 2-2. NADP/NTN Field Observer Report Form.

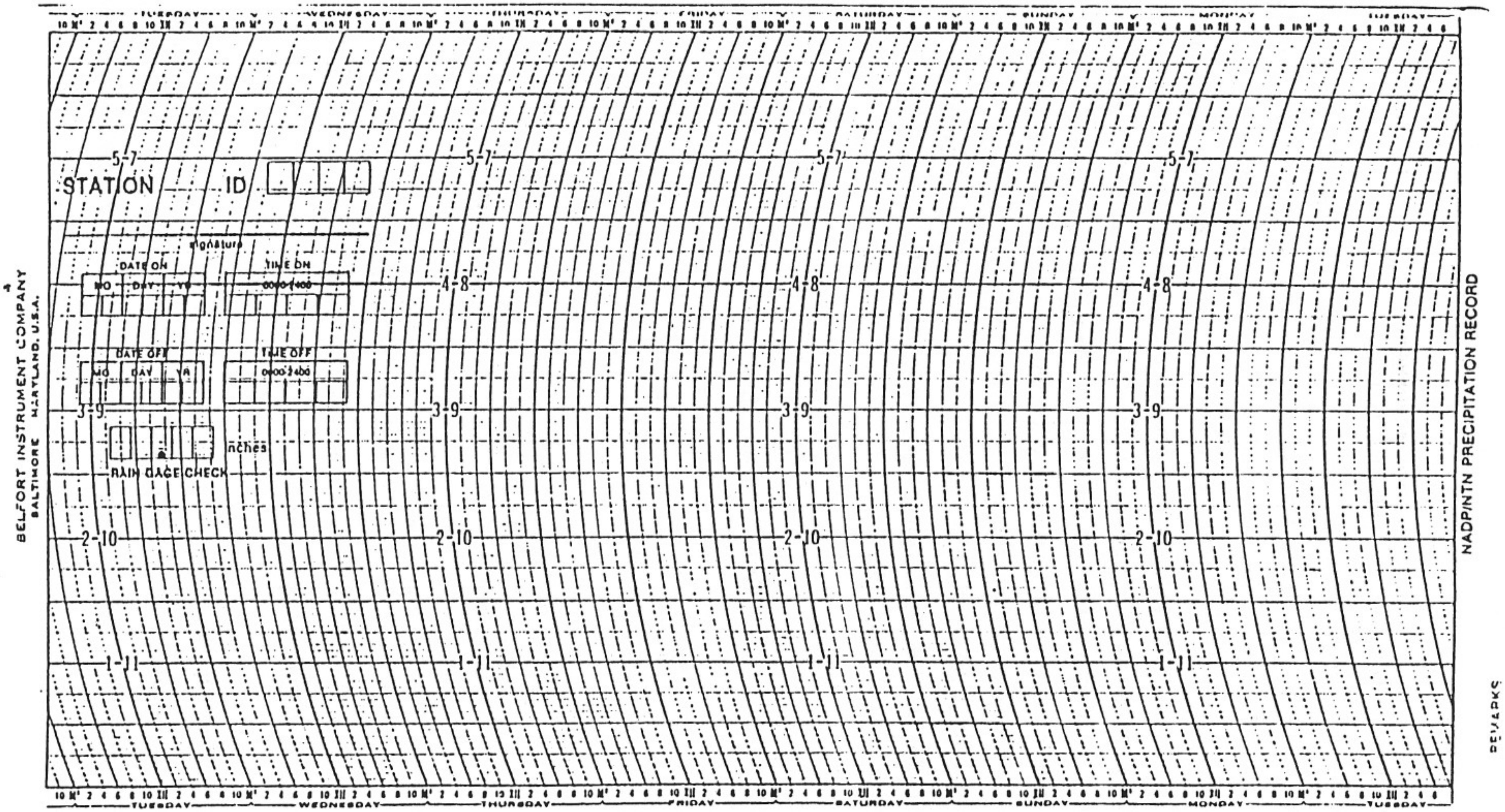

Figure 2-3. Rain Gage Chart

2.8 PERFORMANCE AND SYSTEMS AUDITS

Two federal agencies provide performance and systems audits of field site operations (shown in Table 2-3). The USGS conducts an Intersite Comparison Study to estimate the precision and bias of on-site pH and specific conductance measurements. It also conducts a Blind Audit Program which includes an assessment of the precision and bias related to on-site handling and shipping procedures. Through a contract with Research Triangle Institute, the USEPA carries out a Site Visitation Program in which each site is audited every two or three years for conformance to network protocols. Training, equipment calibration, and other technical services are provided in conjunction with the audit. Details of these external QA programs are provided in Programs and Analytical Methods for the U.S. Geological Survey Acid Rain and Quality Assurance Project (See et al, 1989) and Quality Assurance Project Plan for Systems and Performance Audits of Acid Precipitation Collection Sites -- NADP/NTN and SON Networks (Daum et al, 1988).

Table 2-3

NADP/NTN External Quality Assurance in Support of Field Operations

Program	Frequency	Objective	Agency
Intersite Comparison Study	Twice per year/site	Estimate precision and bias of pH and conductance analysis	USGS
Blind Audit Program	Every 2 years/site, 2 per week through the laboratory	Estimate precision and bias inclusive of sample handling and shipping	USGS
Site Visitation Program	Every 3 years/site	Estimate protocol and conduct systems and performance audits	USEPA

2.9 PREVENTIVE MAINTENANCE/SERVICE

2.9.1 Equipment Checks

The site operation manual (Bigelow and Dossett, 1988) directs field personnel to practice preventive maintenance and to recognize the onset of possible equipment failures.

The following maintenance procedures are conducted regularly.

1. The collector sensor is cleaned at least every 8 weeks with water and a fine brush or towel to prevent a build-up of debris that may cause the collector to stay open too long.
2. A rainfall event is simulated weekly with deionized water to test the collector sensor's switching and heater functions and the motor box's switching and driving functions.
3. The galvanized steel bucket in the rain gage is replaced whenever excessive corrosion is noted.
4. The conductivity cell and pH electrode is replaced whenever the response to the electrode test solution approaches the control limit or when a noticeable change in response occurs.
5. The foam lid seal on the precipitation collector is replaced every 18 months.

2.9.2 Coordination Office Equipment Depot

An inventory of replacement parts for collector and rain gage components that are prone to failure or excessive wear is maintained at the Coordination Office (Olsson et al, 1990). The purpose of the inventory is to minimize the operational lost time that results from equipment failures. Site liaisons at the CAL and the Coordination Office diagnose and respond to equipment malfunctions. In some cases pre-emptive replacement of worn or failing equipment prevents unexpected equipment failures.

2.10 CORRECTIVE ACTION

Tables 2-1 and 2-2 list the performance goals for field site measurements. If results are outside these limits, corrective action is required. Corrective action is also initiated whenever a site departs from the established guidelines and procedures of the network. Procedures for corrective action are as follows:

1. If the site operator notes out-of-tolerance behavior for equipment, he first attempts to correct the problem and makes a notation on the next FORF, along with an estimate of the time affected by the out-of-tolerance condition. If the problem cannot be corrected, the operator contacts the site liaison at the CAL for assistance in correcting the problem.

2. If the need for corrective action is noted at the CAL or Coordination Office during a review of information submitted from a site, the first step is to alert the site operator via telephone or note (Dossett, 1990) so that the site operator may initiate corrective action. If no action is taken and the problem continues,

the CAL or Coordination Office site liaison may call the operator again to discuss the need for corrective action. The network QA manager is also notified of the need for corrective action.

3. If the need for corrective action is noted during a site visit, the site visitor and operator make whatever corrections they can at that time. The site visitor also notifies the site liaisons at the CAL and the Coordination Office of corrective actions taken and the need for further action, if any, through copies of the site survey reports (Section 2.11, no. 3).

In cases where the corrective action cannot be made promptly, or in a case involving personnel and their availability to conduct the weekly sampling according to the network protocols, the matter is handled using the protocol and procedures given in the NADP Remedial Action Plan (see Section 1.5).

2.11 REPORTING AND DOCUMENTATION

Results of the site QA/QC activities are compiled in several types of reports that are distributed to NADP/NTN site sponsors, network management, and to Technical Committee and subcommittee members. The reports, persons responsible for their preparation, and their QA contents are listed below. Data that are summarized in these various reports are also maintained as a permanent part of the NADP/NTN data base (Section 4).

1. Monthly CAL preliminary data printouts are sent to each site operator, supervisor, and the Coordination Office. These reports are described in Section 4.11.1.

2. The publication Quality Assurance Report: NADP/NTN Deposition, Monitoring Field Operations is prepared periodically by the network QA manager. It summarizes QA aspects of field operations.

3. The report, Results of the NADP/NTN Site Visitation Program is prepared by the USEPA after each 3-year cycle of visitations are completed. Other reports of this program include:

   a. Brief Site Survey Report -- a 1-page summary of findings and recommended corrective actions that was prepared on site and left with the supervisor and/or operator. It is also distributed to the network QA manager and the CAL and the Coordination Office site liaisons.

   b. Extended Survey Report -- a 3-page summary that is distributed to the Coordination Office and the CAL site liaison. Photographs, sketches, and maps accompany the copy of the report sent to the Coordination Office. The reports and supporting documentation are archived in site files at the Coordination Office.

c. Site Notebook -- a field notebook that is completed for each site by the site visitor. The information in the notebook is used to complete the Extended Survey Report. Site notebooks are archived in the Coordination Office site files.

d. Annual Summary Report -- a report of QA results from all sites visited in a calendar year. The USEPA publishes and distributes this report to all interested parties.

4. The External Quality Assurance Results for the NADP/NTN is prepared by the USGS and published annually; the report includes summaries of the Intersite Comparison, the Blind Audit Program and Collocated Sampler Program.

SECTION 3
LABORATORY OPERATIONS

3.1 DESCRIPTION

An analytical chemistry laboratory provides the chemical analysis of precipitation samples collected at NADP/NTN sites. The quality assurance plan which follows is the minimum requirement for each laboratory providing service to the program. The Central Analytical Laboratory (CAL) at the Illinois State Water Survey (ISWS) has provided service to the program since its inception in 1978. From March through September 1987, analytical service for approximately 10 percent of the sites were transferred to Environmental Monitoring and Services, Incorporated, Camarillo, California. Prior to that time and since October 1, 1987, all analytical service has been performed at the CAL.

3.2. ORGANIZATION AND RESPONSIBILITIES

The chemistry laboratory is supervised by the laboratory manager who has a Bachelor's Degree in Chemistry or five year's experience in managing a production chemistry laboratory. The functions included in the laboratory are: (a) sample processing and site resupply; (b) sample chemical analysis; and (c) material and data quality assurance. The laboratory has a QA specialist who is responsible for maintaining the QA plan and evaluating laboratory performance. An annual report is prepared on the evaluation results.

3.3. OBJECTIVES AND GOALS

Quality assurance for analytical measurement is a multi-tiered program that includes bench-level quality control, laboratory management-level quality assurance, and external quality assurance monitoring. The overall objective of the program is to produce analytical data whose precision and bias are quantified. As a minimum, the analytical laboratory achieves at least the detection limits listed in Table 3-1, with a maximum allowable bias of $\pm$ 100 percent at the detection limit, $\pm$ 20 percent at 10 times the detection limit; and $\pm$ 10 percent at 100 times the detection limit. Actual detection limits and bias are reported annually in laboratory quality assurance reports. All chemical species are measured on all samples with volumes greater than 10 mL.

Table 3-1

Detection Limit, Bias, and Precision Goals for Laboratory Measurements
(units in mg/L unless noted)

Analyte	Bias/Precision	Detection Limit (DL)
Na^{+}		0.003
K^{+}		0.003
Ca^{2+}		0.009
Mg^{2+}	100% @ DL	0.003
NH_4^{+}	20% @ 10 times DL	0.02
SO_4^{2-}	10% @ 100 times DL	0.03
NO_3^{-}		0.03
PO_4^{3-}		0.02
Cl^{-}		0.03
pH < 5.0	± 0.1/± 0.03	
pH ≥ 5.0	± 0.3/± 0.1	
Specific Conductance		
10-100 µS/cm	± 10%/± 3%	
> 100 µS/cm	± 6%/± 2%	

3.4. SAMPLE PROCESSING AND SITE RESUPPLY

3.4.1. Sample Processing

Field samples sent to the laboratory are processed within 72 hours of their arrival. Each sample is assigned an alpha-numeric designation that includes the type of sample, site identification, and a unique sequential laboratory number for ease of identification. Data sheets used for recording the chemical analyses utilize only this laboratory number for identification purposes. The alpha-numeric designation is also recorded on the Field Observer Report Form (FORF) and is used in the transmittal of data. After completion of analyses, the original FORF, annotated to reflect additional information obtained by the laboratory on the condition of the sample or the handling of the sample in the field or laboratory, is sent to the Coordination Office.

Upon receipt, samples are logged in with all the information on the Field Observer Report Form entered into the computer, together with the sample identification number. In addition, a second copy of the FORF is retained in a site file. Additional information pertaining to the condition of the sample as it arrives at the laboratory is recorded and used in subsequent quality control checks to determine sample representativeness. This information includes an assessment of leakage and gross contamination, compliance with sample bagging requirements, a confirmation of sample weight, and the assignment of an analytical processing code which is based upon the amount of sample in the bucket. The bucket weight is determined, and the sample weight is calculated and recorded before the lid is removed. The draft document Operational Procedure for the Receipt and Check-in of NADP/NTN Samples by the CAL (Morden-Moore 1989) details the incoming sample handling and coding procedures.

When the sample bucket is opened, brief comments are recorded on the visual appearance and presence of odor of each sample. Wet-side samples that are grossly contaminated (contain, for example, a dead mouse or bird, beer can, urine) are logged in at the laboratory and then discarded. Lesser contaminants (twigs, leaves, pine needles, beetles, or bumblebees, etc.) are removed by filtration during routine sample processing.

For all samples, pH and conductance are measured on an unfiltered aliquot, removed from the collection bucket with a clean syringe. If sample remains after this aliquot is removed, up to two additional 60 mL aliquots are passed through a leached, 0.45 micrometer pore-size membrane (cellulose acetate + cellulose nitrate) filter (Millipore™ type HAWP or equivalent) to limit changes in the chemical composition of the aqueous solution. These sample filtrates are then stored in cleaned 60 mL high density polyethylene (HDPE) bottles, until cation and anion analyses are performed. It is from one of these bottles that filtrate is poured for analysis. The second 60 mL HDPE bottled aliquot is stored for a period of at least five years at 4°C without a preservative. Written notification must be made to and concurrence received from the Coordination Office prior to discarding any samples.

Tables 3-2 and 3-3 summarize the chemical measurements performed according to a laboratory type code assigned to wet- and dry-side deposition samples. Samples having different laboratory type codes require different sets of sample processing and measurement steps. Laboratory protocols are closely controlled to preclude errors in recording measurement results.

Table 3-2

Summary Of Laboratory Type Codes Assigned To Wet-Side Deposition Samples

Lab Type	Sample Volume (Vol) Received	Prioritization of Chemical Measurements
T	Vol $\leq$10 mL	as volume permits, first pH and then conductance on unfiltered sample
WA	10mL <Vol <35 mL	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
W	Vol $\geq$35 mL	pH and conductance on unfiltered aliquot; all other ions on filtered aliquot
DA	Vol = 0 mL	50 mL deionized water added to bucket as a leaching agent, lid replaced, contents manually agitated, then left in covered bucket 12-24 hours, subsequent analysis as for W samples

Table 3-3

Summary Of Laboratory Type Codes Assigned To Dry-Side Deposition Samples

Lab Type	Sample Volume	Bucket Treatment
DB	Vol = 0 mL	250 mL deionized water are added to bucket, lid replaced, contents agitated then left in covered bucket 12-24 hours; subsequent analysis as for 'W' samples
WB	Vol > 0 mL	bucket weighed, 250 mL deionized water are added to bucket; lid replaced, contents agitated, then left in covered bucket 12-24 hours; subsequent analysis as for W samples

Each month the laboratory sends every site a report containing information recorded on the Field Observer Report Form. The report includes computer-generated messages concerning errors or potential problems at the site and ion concentration data. Each month the laboratory supplies the Coordination Office with a listing of sites experiencing problems and a brief statement of the problems and resolutions.

3.4.2. Site Resupply

The NADP/NTN is an ongoing monitoring program that requires specific equipment and established protocols to maintain continuity; thus, materials resupplied to the sites by the laboratory must be of identical quality to those being replaced. The following supplies and preparations are provided by the laboratory:

1. Seven shipping boxes (13.5" x 13.5" x 15", with 4" lid, black fiberboard) per site for transporting buckets. Fiberbilt Cases, Inc., 601 West 26th Street, New York, NY 10001-1199, No.14122, style 5Q5.
2. Horsehair mat lining, 2" thick, to line shipping boxes, encased in two polyethylene Zip-lock™ bags.
3. Seven HDPE plastic buckets (3.5 gal.) per site for the collection of atmospheric deposition. Bennett Industries, 515 North First Street, Peotone, IL 60468, white, high-density plastic buckets with snap-on lids. Buckets and lids are cleaned at the CAL according to established protocol (Peden et al, 1986) and are stored in polyethylene bags.
4. One combination pH electrode per site annually. In the event of an electrode malfunction at a site, a replacement electrode is provided (up to one additional per year). Beckman Model No. 39835 or equivalent. Each electrode is tested by the laboratory before being sent to a monitoring site. The essential characteristics of the electrode are that it must respond to standardization with pH 4.00 and 7.00 buffer solutions, and to a check sample of pH 4.3 with a specific conductance of 22 µS/cm. To be acceptable, the electrodes must measure pH 4.3 $\pm$ 0.1 within 5 minutes. Site-returned pH electrodes, when tested and meeting operating requirements, are returned to the replacement stock.
5. Field Observer Report Forms. Triplicate, carbonless forms are purchased from the NADP/NTN Coordination Office.
6. Buffer solutions for pH electrode standardization (pH 4.00 and pH 7.00), as needed by sites. Color coded solutions are required.
7. Check Solutions supplied to sites for verifying pH and specific conductance measurements and for standardizing the specific conductance cell and bridge. Check solutions for pH and specific conductance are prepared to pH 4.3 with

a specific conductance of 22 µS/cm according to Method 150.6 of Peden et al (1986). The standard for conductance measurements is prepared to 75 µS/cm according to Method 120.6 in Peden et al (1986).

8. Rain gage charts (Part No. 5-4046-BI) and ink (No. 10 Purple in 1 oz. squeeze bottle) for Belfort 5-780 Universal rain gages. Belfort Instrument Company, 727 S. Wolfe Street, Baltimore, MD 21231.

9. Replacement foam lid seals for the Aerochem Metrics™ precipitation collector. Lids are provided to each site at 18-month intervals or more often if required due to unanticipated damage. Seals are purchased from the NADP/NTN Coordination Office.

10. Becton-Dickinson™ sterile disposable 20 mL syringes for aliquot removal. One syringe is provided with each bucket sent.

3.5 SAMPLE ANALYSIS METHODS

Analytical procedures are listed in Table 3-4 including the required parameters to be measured, methods to be used, and the lower limits of detection. The analytical methods and practices are described in <u>Development of Standard Methods for the Collection and Analysis of Precipitation</u> (Peden et al, 1986). Before changes or modifications to methods are implemented, a report containing supporting data is submitted and approved by the Chairman of the Subcommittee on Network Operations.

3.6. CALIBRATION PROCEDURES

Standards preparation and instrument calibration are among the most critical procedures in laboratory quality control. Several options are available for quality control of the preparation of stock standard solutions. The laboratory selects at least two of the following procedures as standard practice, depending on the standards being prepared and their cost effectiveness: (1) arrange for independent laboratory confirmation of each standard; (2) obtain confirmation by an independent analytical procedure within the laboratory (CAL); (3) prepare two lots of each standard using independent analysts in the same laboratory and compare; (4) compare the results of new standard solutions to those obtained with certified reference solutions; or (5) compare the results of new standard solutions to those obtained with prior standards. All standard solutions are reformulated at or before the 6-month lifetime of the solutions. The validity of the calibration procedures is checked in interlaboratory programs as described in Section 3.11.

Instrument calibration procedures are documented for each measurement in Peden et al (1986). The frequency of calibration may vary with the measurement but is not less than once per day.

Table 3-4

Analytical Methods for Constituent Determination

Constituent	Analysis Method[1]	Method Number	Lower Limit of Detection
Na^+	AAS	200.6	0.003 mg/L
K^+	AAS	200.6	0.003 mg/L
Ca^{2+}	AAS	200.6	0.009 mg/L
Mg^{2+}	AAS	200.6	0.003 mg/L
NH_4^+	AC	N/A[2]	0.02 mg/L
SO_4^{2-}	IC	300.6	0.03 mg/L
NO_3^-	IC	300.6	0.03 mg/L
PO_4^{3-}	IC	300.6	0.02 mg/L
Cl^-	IC	300.6	0.03 mg/L
Specific Conductance	EL	120.6	0.1 µS/cm[3]
pH	EL	150.6	0.01 units[3]

[1]AAS = Atomic absorption spectrophotometry, AC = Automated colorimetry, IC = Ion chromatography, EL = Electrometric.

[2]Ammonium methodology was recently switched from segmented flow (SFA) to flow injection (FIA). Though equivalency has been established for these two implementations of the same chemistry no separate method designation number has been established.

[3]Not the lowest value measured, but rather the lowest difference able to be detected between two measurements; a measure of sensitivity.

3.7. RECORD KEEPING

All laboratory personnel have access to records for review and assessment of problems. Paper records are maintained for no less than one year following formal publication in tle NADP/NTN data reports. All laboratory log books are archived at the CAL for the duration of the contract.

3.8. QUALITY CONTROL

Precipitation samples are typically characterized by a low dissolved solids content (<20 mg/L) resulting in a highly unbuffered system. Because of this, a quality-assurance program for the chemical analysis of precipitation samples requires stringent laboratory conditions and careful control over all aspects of the analyses. Each step in the analytical flow chart shown in Figure 3-1 is a potential source of contamination and must be constantly monitored to ensure that the final determinations are not adversely affected by any processing steps. The quality control procedures herein have been developed to provide the necessary checks at all processing stages.

3.8.1 General Laboratory Procedures

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 exclusively for sample storage prior to analysis. Borosilicate glass or HDPE containers are used for standard solution preparation and storage. All volumetric glassware is Class A under American Society for Testing and Materials (ASTM) Standards E-287 for Burets, E-288 for Volumetric Flasks and E-969 for Volumetric (transfer) Pipets (Annual Book of ASTM Standards, Vol. 14.02). Dilutions and standards are prepared using both fixed and variable volumetric pipets. The bias and precision of the pipets are monitored by dispensing distilled water aliquots onto a semi-micro analytical balance accurate to 1×10^{-5} gram. Disposable plastic pipet tips, if used, are rinsed copiously with DI water before use to remove surface impurities.

Membrane filters (Millipore™ type HAWP, 0.45 µm, or equivalent) used to separate the dissolved and suspended fractions in precipitation, are leached with 300 mL of deionized water prior to use. Filter blank aliquots are collected and analyzed weekly for all 11 parameters to ensure that the filtration procedure does not contribute any significant contamination to the precipitation sample. In addition, synthetic precipitation solutions are submitted randomly for analysis to assess the sorption and leaching phenomena of the filters. Recovery percentages are calculated for these solutions.

Laboratory deionized water used for cleaning and solution preparation purposes has a specific conductance <1.0 µS/cm. Deionized water samples are collected weekly and analyzed to verify water purity.

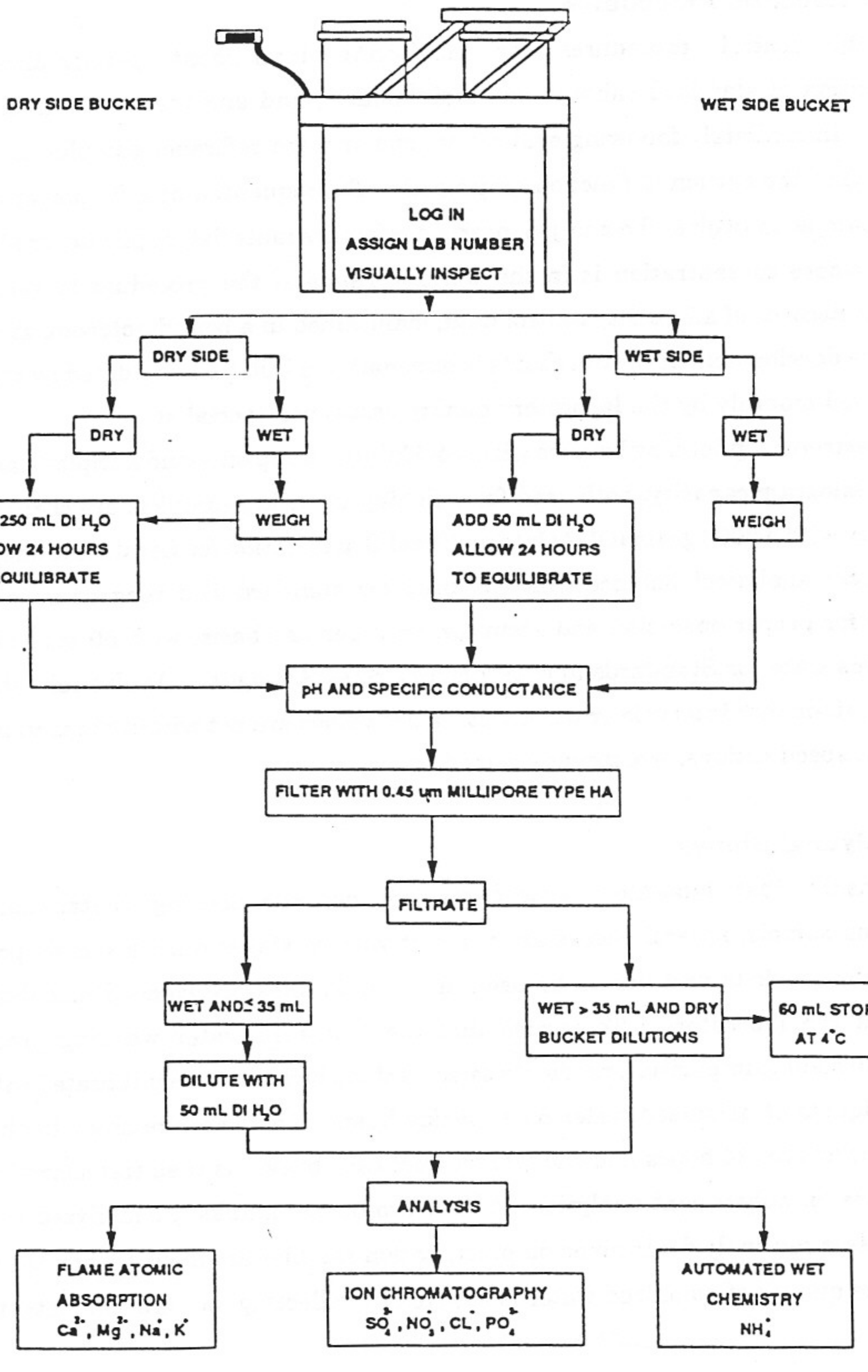

Figure 3-1. Sample Processing Flow Chart

3.8.2. Instrumental Procedures

Quality control procedures for monitoring instrument performance involve documentation of standard calibrations, maintenance, and analyses of certified reference materials. Immediately following calibration, one or more reference samples are analyzed to ensure that the system is functioning properly. Subsequently, at a frequency of not less than one sample in twelve, the analyst inserts a reference material, duplicate, or single-point standard whose concentration is in the working range of the procedure to verify correct operation. Records of all quality control data, maintained in a bound notebook at each work station (the development of control charts is optional), are initialed and dated by the analyst, and reviewed monthly by the laboratory quality assurance specialist.

An electronic top-loading balance with a 4-5 kilogram capacity and a triple-beam balance with a 20 kilogram capacity, both used for weighing incoming samples, are checked weekly for accuracy with a 2000 gram IOLM (International Organization for Legal Metrology) weight. A semi-micro analytical balance which is used for standard and reagent preparation is monitored for proper operation and accuracy, on a per use basis, with 50 mg and 100 mg National Institute for Standards and Technology class S weights. Analytical balances are serviced at six-month intervals or when test weight values are not within the manufacturer's instrument specifications, whichever occurs first.

3.8.3. Analytical Blanks

To ensure that laboratory procedures are not contributing contaminants to a precipitation sample, several checks are made at various stages during sample processing. The collection buckets and lids to be used at the field sites are cleaned and individually wrapped at the laboratory. To ensure that the deionized water washing procedure is removing all soluble impurities, randomly selected clean buckets are equilibrated with 50 and 150 mL aliquots of deionized water on a weekly basis. The water remains in the sealed, inverted buckets for 24 hours and one aliquot from each bucket is then transferred to 60 mL HDPE bottles for subsequent analysis. At least two bucket blanks are analyzed each week. All parameters routinely determined on precipitation samples are measured on these bucket blanks. The quality of deionized water is assayed by collecting 50 mL aliquots in HDPE bottles. These water blanks are not filtered but are otherwise handled as though they were precipitation samples. At least one deionized water sample is collected and analyzed weekly.

Filter blank solutions consist of aliquots of filtered, deionized water collected on a weekly basis during a normal filtration. The blanks consist of two sequential 50 mL aliquots collected after the filter has been leached with 300 mL of deionized water. At least two aliquots are analyzed each week.

If two or more concentration values for any blank solution exceeds the historical 90th percentile levels for the analyte, more blank solutions are analyzed to determine if the values in question are random or persistent. If the problem persists and the additional blanks indicate a continuing condition, further action takes one of several forms depending on the type of blank:

1. Bucket lid o-rings are the main source of contamination in bucket blanks. High blank values are corrected by altering the leaching and washing procedure until the analyte concentrations are reduced. The manufacturer is contacted to see if the manufacturing process can be altered to lessen the problem.
2. In the event of elevated deionized water blanks, treatment equipment is inspected and repaired if necessary so that the resulting water quality is within specifications.
3. If a series of membrane filters exhibit contamination, another package or a different lot number is opened and the leachates analyzed. The laboratory environment, including filtration equipment and personnel, are also evaluated as sources of contamination. If the equipment is the apparent source, the cleaning procedure is made more rigorous. If personnel are the source, the technique is revised to reduce blank levels back to detection limit concentrations.

3.8.4. Replicate Samples

Two percent of the sample load, excluding standards and reference materials, consists of replicate samples (split at the laboratory). The replicates are individually numbered and are physically separated in the sample set for analysis. Results of replicate sample analyses are computed on a biweekly basis and used to produce within laboratory precision statistics for all measured parameters.

3.8.5. Data Verification

In addition to the quality control measures implemented during sample handling and processing, precipitation sample data are subjected to computer 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 and 5 percent of the entries are spot checked by a second individual. Manually-entered and computer-captured data are merged into a single file where control checks (defined in the computer programs), ensure that the data are in the proper form and that all necessary information is provided. The ionic balance is calculated for each sample. The percentage difference between calculated and measured specific conductance is also tabulated. Samples are computer selected for reanalysis based on the predetermined control limits for ion balance and specific conductance differences (Table 3-5). A complete reanalysis is carried out on all samples selected. Original versus repeat values are compared to identify outliers which require further investigation. Values are changed only when it can be determined that the original values were in error or where repeated checks suggest the original analysis was contaminated. If values are changed, the original, repeat, and corrected final data are all maintained in the computerized data base. Criteria for selection of samples for reanalysis are as presented in Table 3-5.

The final selection for reanalysis includes the random addition of 1 percent of the monthly sample load. A random number table is used to add to the reanalysis list those precipitation samples that correspond to 20 consecutive random numbers. If any of the 20 have been selected previously because of ion balance or conductivity balance criteria, they are excluded from the random selection and replaced by the next consecutive random number.

Selected samples that are not coded laboratory type W (those with less than 35 mL of sample) or that did not originate from a field site (i.e., an internal or external blind quality assurance sample) are also excluded and replaced by the next suitable sample. This random selection results in a 1 percent addition of samples to the reanalysis list for an overall selection of 5-7 percent.

3.9 PERFORMANCE AND SYSTEMS AUDITS

Internally, current information on the characteristics (e.g., precision, bias, detection limit) of analytical methods is provided by a continuous quality assurance monitoring

Table 3-5

Sample Reanalysis Criteria

a. Ion Percent Difference

If: (Anions + Cations) (µeq/L)	Reanalyze when: [(Anions - Cations/(Anions - Cations) x 100]
<50	> ± 60%
≥50 but <100	> ± 30%
≥100	> ± 15%

b. Conductance Percent Difference

The Conductance Percent Difference (CPD) is calculated by subtracting the measured conductance from the calculated conductance,[1,2] multiplying the difference by 100, and dividing the product by the measured conductance. Samples are reanalyzed if the CPD is outside of the range from -40% to +10%.

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[1]Calculated Conductance (µS/cm) = [(H^+)(350) + (HCO_3^-)(44.5) + (Ca^{+2})(59.5) + (Cl^-)(76.3) + (Mg^{+2})(53.0) + (K^+)(73.5) + (Na^+)(50.1) + (NO_3^-)(71.4) + (SO_4^{-2})(80.0) + (NH_4^+)(73.5) + (OH^-)(198) + (PO_4^{-3})(69.0)] ÷ 1000 where ionic concentrations are expressed in microequivalents per liter.

[2]Standard Methods for the Examination of Water and Wastewater, 16th Edition (Franson (ed), 1985) with update conductance factors from the 70th edition of the CRC Handbook of Chemistry and Physics (Weost (ed), 1989).

program operated by the laboratory quality assurance specialist. The program includes "blind" insertion into the normal sample flow of split samples (Section 3.8.4), samples for delayed reanalysis (Section 3.8.5), reference samples, and standard solutions. The frequency of analysis of QA samples is not less than 1 sample in 20.

The laboratory also participates in a formal external quality assurance program consisting of the following: a blind sample audit, an interlaboratory comparison, and periodic on-site reviews. In addition, the laboratory participates in interlaboratory programs sponsored by the American Society for Testing and Materials, the World Meteorological Organization, and the U.S. Environmental Protection Agency. The purpose of this cooperation is to provide an information base for comparing analytical results to those from other laboratories.

The Blind Audit Program is operated by the USGS. The program uses reference samples, measured and certified by the USGS, that are sent to specific sites according to an agreed upon schedule. The site treats the blind audit sample as if it were a precipitation sample, submitting it to the laboratory in a clean sample bucket. The goal of the program is to add at least two weekly audit samples of known concentration to the analytical process, blind to the laboratory's personnel. Additionally, a remaining portion of the bottle from the same sample is analyzed by the laboratory, after a delay. The data generated by this program are reported along with regular sample data.

The Interlaboratory Comparison Program, also operated by the USGS, involves four laboratories: the Water Quality Laboratory of Environment Canada, Burlington, Ontario; the Central Analytical Laboratory at the Illinois State Water Survey and the USEPA National Dry Deposition Network's (wet deposition samples) contract laboratory, Hunter Environmental Services, Inc. The NADP/NTN laboratory(s) participate in the intercomparison program. The purpose of this program is to provide bias and variance estimates of the analytical methodology at each laboratory. Intercomparisons on six natural rain water or reference samples are performed every two weeks. Deionized water blanks provided by the USGS, are also included to test for false positive values. Results of this program are sent to the USGS Quality Assurance Project Manager.

On-site reviews of the CAL are conducted biannually by members of the Subcommittee on Network Operations. The reviews are designed to familiarize members of the committee with the CAL operations and to review the CAL's operating procedures in light of changes of objectives, program goals, and recent developments in deposition monitoring techniques. Review team members consist of the subcommittee chairman and others selected by the subcommittee membership.

Results of performance and system audits are reported by the agency initiating the audit.

3.10. PREVENTIVE MAINTENANCE/SERVICE

A maintenance schedule is established for each instrument and included in the instrument's log book. A record of all scheduled and unscheduled maintenance is kept. The record includes, at a minimum, the date, time, servicing person, and nature of the service.

The log is reviewed periodically by the laboratory manager to determine that adequate spare-parts inventories and service agreements are in place.

3.11. CORRECTIVE ACTION

If the results from the analysis of quality control or quality assurance samples exceed the established control limits, corrective action is taken. Control limits for the laboratory quality control samples are $\pm$ 3 standard deviations from the certified or theoretical concentration for any given analyte. Standard deviation values are based on method performance data documented in Peden et al (1986). The laboratory's quality assurance specialist is responsible for ensuring the timely solution of identified problems within the analytical laboratory. Problems identified by the external quality assurance program are reported to the network quality assurance manager who initiates, tracks, and documents the remedial actions.

3.12. REPORTING AND DOCUMENTATION

Formal reports are submitted every two months to the laboratory manager by the laboratory quality assurance specialist. These reports include the results and evaluation of internal quality assurance program analyses and documentation of problems and associated corrective actions during that period. The reports also include documentation of method changes. These reports are summarized annually by the laboratory manager and submitted to the Coordination Office. Reports of the external quality assurance programs are provided to the Coordination Office annually by the USGS. The Coordination Office publishes an annual quality assurance report for the entire program.

Documents required to support the quality control/quality assurance activities of the analytical laboratory consist of three log books, two operations manuals, and a laboratory quality assurance plan. Each log book entry is initialed and dated and the books are reviewed at least quarterly by the laboratory quality assurance specialist. These documents are:

1. Analyst's Log Book -- maintained by each analyst and contains a record of working standards preparation, reference sample results and daily notes.

2. Instrument Log Book -- maintained for each instrument at the work station and contains the maintenance schedule, record of performance of scheduled

and unscheduled maintenance, daily instrument settings and calibration data, and observations.

3. Standard Solution Log -- contains all information pertinent to preparation of stock standard solutions, including all weights and volumes, confirmatory analyses, and a shelf life table.

4. Sample Handling SOP -- gives the procedures for receiving and preparing samples for analysis and permanent storage, cleaning of sample containers and lids, and packaging and shipping procedures. It is reviewed and approved at least every three years by the Subcommittee on Network Operations.

5. <u>Development of Standard Methods for the Collection and Analysis of Precipitation</u> (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 approval of the chairman of the Subcommitte on Network Operations.

6. Laboratory Quality Assurance Plan -- provides the laboratory-specific details for each topic contained in the Laboratory Operations section of the Quality Assurance Plan (this document). The plan is reviewed and revised at least annually and copies are provided to the chairman of the QA Steering Committee and the NADP/NTN Coordinator.

SECTION 4
DATA MANAGEMENT OPERATIONS

4.1 DESCRIPTION

The data management task involves collecting, entering, transferring, verifying, validating, summarizing, and reporting network data. Network data include descriptive and historical information about each network site, all field and laboratory data, quality assurance documentation, and summaries and reports of site and network operations.

Data records from NADP/NTN monitoring sites, the Central Analytical Laboratory, and external auditing agencies are transferred to the Coordination Office. These data are a mixture of primary data records, summaries of primary data, and results of data quality evaluations that were performed as a part of routine network quality control. The records may include paper or hardcopy documents as well as electronic media, such as computer tapes, disks, and electronic mail messages.

4.2 ORGANIZATION AND RESPONSIBILITIES

Responsibility for data management is distributed among monitoring sites, the CAL, the Coordination Office, and the federal agencies conducting external program audits. Final responsibility for data management activities resides with the Coordinator. All data management procedures are subject to approval by the NADP Technical Committee.

Figure 4-1 illustrates the relationship among the various data management groups and demonstrates the exchange of information that ultimately results in the creation of the network data base. Responsibility for the integrity of transferred data passes to the receiving organization when both the transmitting and receiving organization agree on the content of the passed data. Table 4-1 lists the individuals responsible for data management in each data group.

4.2.1 NADP/NTN Monitoring Sites

NADP/NTN field sites submit a Site Description Questionnaire (Bigelow, 1984) documenting the sites' location, administration, instrumentation, and emission source profile to the NADP/NTN Coordination Office. In addition, each site submits a weekly FORF (Figure

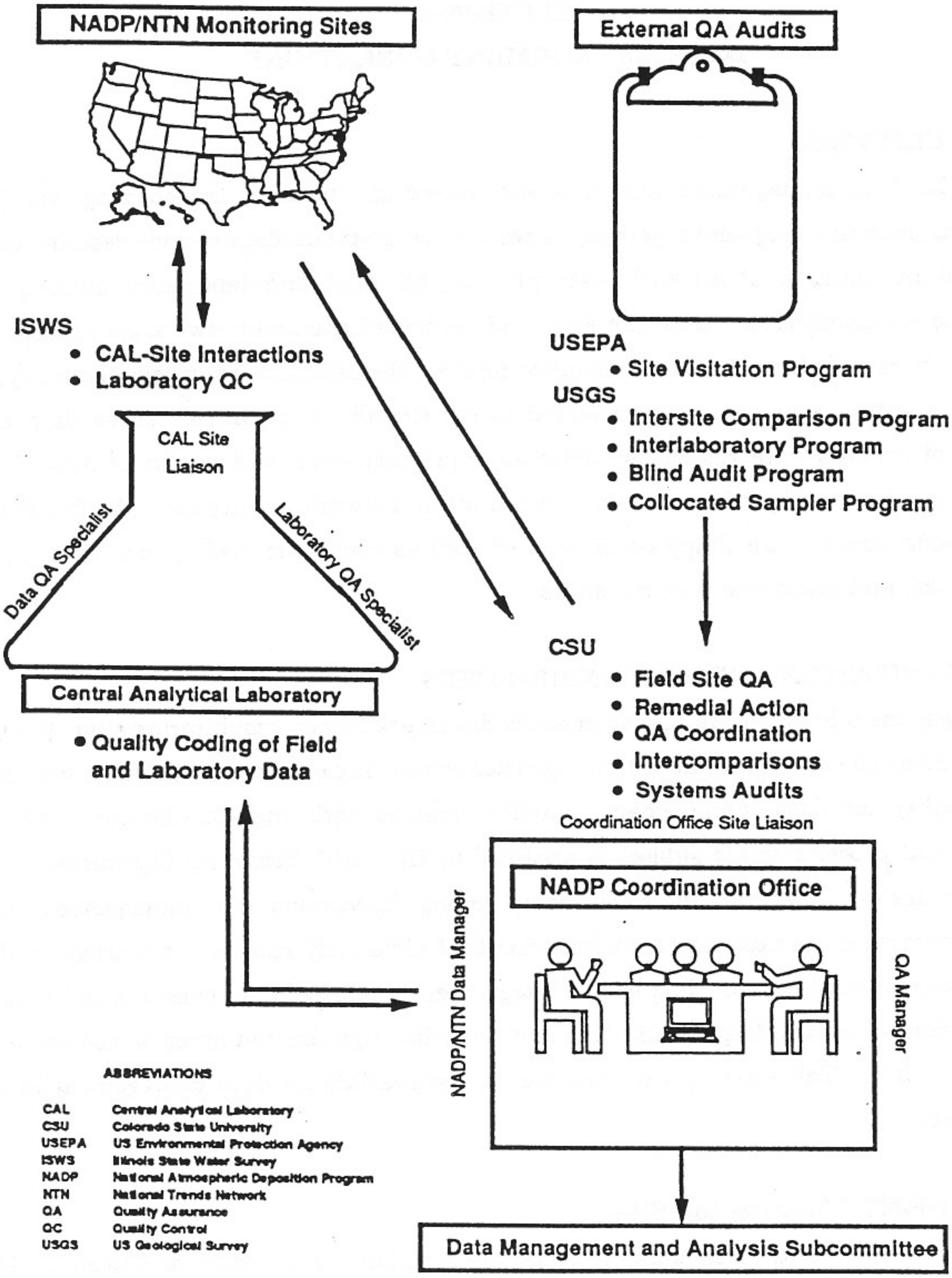

Figure 4-1. Organization of Data Management Activities

2-2) that contains information about the sample submitted to the CAL. This information includes a definition of the sampling period, a report on the sample condition, weather information, and the results of field chemistry and QC checks performed. The FORF is accompanied by a recording rain gage chart (Figure 2-3). The site operator is responsible for submitting data to the Coordination Office and the CAL. The operator is also responsible for remedying incomplete or inaccurate site data.

4.2.2 The Central Analytical Laboratory (CAL)

The CAL is the main technical contact point for monitoring sites and is the laboratory conducting the chemical analysis of the network samples. The CAL is also responsible for verifying and validating weekly site data submitted via the FORF and rain gage chart, and for summarizing the results of all site-laboratory interactions. In addition, the CAL is responsible for the initial assessment of data quality.

Table 4-1

List of Data Management Personnel by Organization

Monitoring Site	Central Analytical Laboratory	External Auditing Agencies	NADP/NTN Coordination Office
Site operator	CAL Director	Agency Representative	Coordinator
	Data Quality Assurance Specialist		Associate Coordinator
			Coordination Office Site Liaison
	CAL Site Liaison		NADP/NTN Data Base Manager
	CAL Data Base Manager		Data Technician(s)
	Programmer(s)		Programmer(s)
	Data Clerk(s)		Quality Assurance Manager
	Laboratory Manager		
	Laboratory Quality Assurance Specialist		
	Laboratory Analysts		

The CAL director has overall responsibility for the laboratory's data management activities. The CAL site liaison has responsibility for information exchange between the CAL and the site operator and additionally, is responsible for quality control at the monitoring stations. Quality control of data management activities in the laboratory is the responsibility of the laboratory QA specialist. The laboratory manager has responsibility for transferring laboratory data from the laboratory analysts to the CAL data base manager. The CAL data base manager is responsible for all additions, deletions, and updates to the CAL-NADP/NTN data and other than the director, is the only person to have access to the data files. The validation of the merged field and laboratory data set is the responsibility of the data QA specialist.

The CAL site liaison, the CAL data base manager, and the data QA specialist report directly to the CAL director. The laboratory QA specialist reports to the laboratory manager who reports to the CAL director. The programmer(s) and data clerk(s) assist the director and laboratory manager in entering and transferring data and in implementing and writing computer programs and software packages that handle network data.

4.2.3 External Auditing Agencies

External QA program data are submitted to the Coordination Office by the auditing agencies. Results of these audits are also returned to each site or to the CAL, as appropriate. The auditing agency is responsible for the quality and content of the data.

4.2.4 NADP/NTN Coordination Office

The Coordination Office is the principal data repository for the network. As such, it is responsible for ensuring that network data meet the data management needs of the National Atmospheric Deposition Program and the National Trends Network. These needs are specified and approved by the NADP Technical Committee. Data requirements include ensuring that both data between stations and within a single station's historical record are comparable; ensuring that the transformation of data is done correctly during both the special and routine reporting of network data; and ensuring that all aspects of the network's operations are thoroughly documented. This office is also responsible for the overall coordination of data management practices, including the final certification of network data and data products. Finally, the office is responsible for updating network data to comply with decisions made by NADP subcommittees.

The associate coordinator at the Coordination Office has overall responsibility for network data management activities. The NADP/NTN data base manager is responsible for receiving, verifying, transforming, and updating network data submitted by the site operators, the CAL, and the auditing agency representatives and has overall responsibility for documenting data completeness, and summarizing and reporting data. The Coordination Office site liaison is responsible for information exchange between the sites and the Coordination Office. This includes documenting site operational problems, changes in site configuration and location, and maintaining records of remedial actions at sites.

The QA manager is responsible for final validation and characterizations of network data, accumulation of network documentation, and assessment of data quality. Because the QA manager has overall responsibility for data quality, he is responsible for limiting access to network data.

The programmer(s) and data technician(s) assist the NADP/NTN data base manager and QA manager in entering, transferring, and transforming data. They also assist in implementing software packages and writing computer programs that manipulate network data. The associate coordinator and the QA manager report to the coordinator. All other data management staff report to the associate coordinator.

4.3 OBJECTIVES AND GOALS

The achievement of the overall objectives of the NADP/NTN monitoring program (Section 1.4.2) is largely dependent upon the network's success in managing its data. With this in mind, the general network data management objective is to provide the monitoring program with a thorough and accurate accounting of all activities and information gathering undertaken by the network. More specific objectives, along with the goals for achieving them, are given below:

4.3.1 Data Completeness

The objective of the data completeness goals is to provide the network with continuous records of all scheduled monitoring at each site on an annual basis. The specific goals are as follows:

1. Accountability for 100 percent of the weekly sampling periods at all network sites.
2. Acquisition of rainfall records for a minimum of 90 percent of the days in an annual period at each site.
3. Collection of valid samples from a minimum of 75 percent of the sampling days in an annual period at each site.
4. Representation by valid samples of a minimum of 75 percent of the precipitation volume reported in an annual period.
5. Acquisition of 100 percent of external auditing agency results.

4.3.2. Data Transformation and Verification

The objective of the data transformation and verification goals is to ensure that original data is not unknowingly systematically changed as it is transferred from field instrumentation and observations to final reports. The specific goals are as follows:

1. Better than 99 percent accuracy in data entry from standard forms to computerized files.
2. Better than 99 percent accuracy in transferring data via computerized media.
3. No loss or gain in significant digits or detection limits when data are transformed by or transferred between responsible organizations (Figure 4-1).
4. No changes in field, laboratory, or audit data other than unit conversions without permanent documentation.

4.3.3. Data Validation

The objective of data validation is to qualify network data in a manner that will facilitate the understanding and use of the data. Specific goals are as follows:

1. Data and summaries of data made available through the program contain information that identifies instances where the network's sampling or analysis protocols have been violated.
2. All changes in data quality requirements, including data screening and flagging protocols, are applied retroactively to all data to the extent possible.
3. The validity of network data is unaffected by changes in computer systems and software and data management procedures used in the network.

4.3.4. Documentation

The documentation objective in the NADP/NTN monitoring program is to provide users of NADP/NTN data with a clear understanding of both the data gathered and methods used to collect network data. Specific goals to achieve this objective include:

1. Complete documentation of the monitoring station location, administration, equipment, and potential emission sources.
2. Time-stamped records of all changes to and usage of standard forms, computer hardware, software and programs, and standard reports.
3. Original standard field forms and network data stored in perpetuity.
4. Documentation of all validation coding and data flags assigned to each sample collected.
5. Complete documentation of external audit methods and results.

4.3.5 Data Reporting

Data reporting objectives are to present a maximum amount of network data to scientific users in the minimum amount of time and to keep the reporting formats of network data as objective as possible. The following specific goals are used to achieve these objectives.

1. Site operators submit standard field documentation to the CAL within 48 hours after removing the sample from the field.
2. Site operators receive a preliminary report of field data and laboratory chemical analysis results within 60 days after the sample is submitted.
3. The CAL transfers all required final data and supporting documentation to the Coordination Office within four months of sample submission.
4. Quality, scientifically sound data from each site are available to the public within one year of field sampling.
5. Requests for network data are filled within one week.
6. Special data reports and summaries adhere to the same data quality requirements as routinely scheduled network data reports.

4.4 DATA COLLECTION, ENTRY, TRANSFER, AND TRANSFORMATION

4.4.1 Site Description Records

The Instruction Manual: NADP/NTN Site Selection and Installation (Bigelow, 1984) contains instructions for completing the NADP/NTN Site Description Questionnaire. This questionnaire provides the initial documentation for site location, administration, equipment, and emission source records.

The site operator submits this information to the Coordination Office site liaison for review and data entry into an ASCII (American Standard Code for Information Interchange) computer file, (one per site). Unit conversions are performed and typographical errors are corrected during this data entry step. Frequently used portions of these files are then transferred into a data base management system (DBMS), where reporting and summarization applications are built. The standard format for these files and the instructions for their entry are discussed in Procedures Manual: Evaluating and Documenting NADP and NTN Monitoring Sites (Reuss et al, 1990).

Original site documentation is maintained at the Coordination Office in storage files, one per site.

4.4.2 Weekly Field Information

The Instruction Manual: NADP/NTN Site Operation (Bigelow and Dossett, 1988) contains the site operator's instructions for completing the weekly FORF and for interpreting the weekly rain gage chart. When completed, these two documents are forwarded to the CAL.

At the CAL, each FORF and rain gage chart is coded with a unique, alpha-numeric laboratory identification (See Section 3.4.1). The information from the completed FORF is entered into a DBMS that resides on a dedicated CAL personal computer (Morden-Moore, 1989). Additional information describing sample leakage, gross contamination, compliance with sample bagging requirements, confirmation of sample weight, and laboratory pH and conductance measurements are also entered into the DBMS.

The original FORF is next sent to an independent data entry group, where the contents are entered into computer files on a second CAL computer. A computer program compares this information to the previous DBMS entries and identifies any discrepancies. Discrepancies are resolved manually by the CAL data base manager. The verified results of this check become a preliminary data base of field data. Specific data-entry procedures used at the CAL are documented in detail in Operational Procedures for the Management of the NADP/NTN/CAL Data Base (Douglas and Bowersox, 1989) and Operational Procedures for the Computer Entry of Field Observer Form (FORF) Data, Chemical Analytical Data, and Descriptive Information at the CAL of the NADP/NTN (Morden-Moore, 1990).

4.4.3 Chemical Analysis Results

For laboratory instrumentation using automated data-acquisition methodologies (SO_4^{2-}, NO_3^-, PO_4^{3-}, Cl^- and NH_4^+), instrument signals are converted directly to concentration data using calibration rules supplied in each analyst's SOP (Peden et al, 1986). The rules are programmed by the manufacturer or the CAL computer programmers into an integration unit (or computer) that performs the necessary transformations using the rules and results from the analysis of calibration, blank, and other QA solutions measured by the laboratory analysts. Concentration data are written to a computer disk or file, where it is reviewed by the laboratory analyst. After this review, results are transferred to the CAL data base manager.

Methods not using automated data-acquisition methodologies (Ca^{2+}, Mg^{2+}, Na^+, K^+, pH and conductance) rely on the manual transcription of instrument output by the laboratory analyst. Standard data forms containing the transcribed results are given to the CAL data base manager and then to an independent data entry group, which double enters the results into computer files. Any errors detected during this keystroke-by-keystroke verification step are corrected. These verified files are then merged with preliminary field data to form the preliminary NADP/NTN data base.

In both automated and manual data acquisition, laboratory analysts are responsible for the correct entry and transformation of instrumentation output. The laboratory manager is responsible for submitting the results to the CAL data base manager. Sections 3.4.1, 3.7, 3.8.5 and 3.13 of the Laboratory Operations portion of this document further describe data management practices related to chemical analysis results.

4.4.4 Merged Field and Chemical Analysis Data

The CAL data base manager maintains a data base of preliminary field and laboratory data. Any subsequent editing, including transforming of local date and time information to Eastern Standard Time (EST), is performed by computer programs or DBMS commands initiated by the CAL data base manager.

Preliminary data that have been validated by the data QA specialist are transferred electronically to the Coordination Office. During this transfer, time fields are transformed from EST to Greenwich Mean Time (GMT) and precipitation data are transformed from inches of precipitation to millimeters of precipitation. The procedures used by the CAL data base manager are documented in Douglas and Bowersox (1989). Computer programs used by the CAL are documented in Computer Hardware and Programs, Procedures, and Software Used by the NADP/NTN/CAL Data Management Group (Dzurisin and Bowersox, 1990).

At the Coordination Office, computer programs reformat the data for QC testing and then enter it into a DBMS. During this procedure, data-quality coding is translated by computer into a more general set of NADP subcommittee-approved record note codes and data validation codes. The translated codes categorize weekly data in a way that the NADP Subcommittees deem compatible with appropriate uses of the data. Additional note codes and data validation codes may be added to permit selected retrievals of data, or to identify sites or sampling intervals that are not used in making routine network data interpretations. The assignment of these codes is based on information provided by the CAL, from site audits, and from the review of information supplied to the Coordination Office.

Computer programs also calculate the Julian date and day of the week from the date and GMT data fields, and they maintain these along with a last-modified-date as permanent additions to the data base. Seasonal (monthly, quarterly, and annual) averages and completeness summaries are calculated from the primary records residing in the DBMS and are stored as additional, permanent network data with their own last-modified-date in the DBMS. Specific data-transformation procedures used at the Coordination Office are documented in Procedures Manual: Weekly Data Processing (Scott and Reuss 1989a). Computer programs and descriptions of file formats reside in a single directory in the computer system at the Coordination Office.

4.4.5 External Audit Information

Data collection, data entry, and transfer of external audit information from auditing agencies (See et al, 1989; Daum et al, 1988) to the monitoring network takes place through the Coordination Office. The NADP/NTN data base manager oversees the data entry and transformation of information into the standardized formats used in the computer files and DBMS tables of the network data base. The standard format for these files and the instructions for their entry are contained in three Coordination Office draft documents titled Procedures Manual: Processing of NADP/NTN Site Visitation Information (Olsson and Reuss, 1989); Procedures Manual: Intersite Comparison Program (Reuss, 1989a); and Procedures Manual: NADP/NTN Blind Audit Program (Reuss, 1989b).

4.5 DATA VERIFICATION AND VALIDATION

4.5.1 Site Description Records

Once the Site Description Questionnaire information is entered into computer files at the Coordination Office, the Coordination Office site liaison reviews the files for completeness and format consistency. All information is compared to the maps, sketches, and photographs submitted with the questionnaire and to the most current emission inventory available to the Coordination Office. Discrepancies and omissions are resolved with the assistance of the site personnel. The date of the most recent review appears at the top of each file, along with a date signifying when the file was last modified. Specific procedures for verifying and validating site descriptive information is contained in Procedures Manual: Evaluating and Documenting NADP and NTN Monitoring Sites (Reuss et al, 1990).

4.5.2 Weekly Field Information

Immediately after the data from the FORF have been entered into the CAL DBMS, the original rain gage chart and a second copy of each FORF are forwarded to the CAL site liaison. The CAL site liaison critically reviews each form for completeness, consistency, and compliance with the sampling protocols of the network, resolving any discrepancies with the site operator whenever possible. During this review the FORF and rain gage data are verified. Corrections to these data and the source of the correct information are then entered into a computer file by the CAL site liaison. A validation code, known as a protocol code, is also assigned to each deposition sample to indicate departures from standard sample collection procedures that may have compromised sample integrity. These checks and protocol codes are detailed in Stensland et al (1983), Bowersox (1985) and the ISWS draft document, Operational Procedures for the Review of NADP/NTN Data by the CAL Site Liaison (Dossett, 1990).

The CAL site liaison transfers the file containing the corrections and protocol codes to the CAL data base manager, who then runs a computer program that incorporates the changes into the preliminary data base of field information. The CAL site liaison additionally maintains, for reference purposes, a record of all oral and written communications with site personnel. Computer file structure and programs used in data verification and validation at the CAL are documented in ISWS documents by Douglas and Bowersox (1989) and Dzurisin and Bowersox (1990).

4.5.3 Chemical Analysis Results

The verification and validation of chemical analysis results is described in the Laboratory portion of this Quality Assurance Plan (Section 3.0).

4.5.4 Merged Field and Chemical Analysis Data

The data QA specialist receives the FORFs, rain gage charts, and all other accumulated information relevant to the validation of site records. Level codes are assigned to samples that were contaminated or that were identified as having been handled in a manner inconsistent with field or laboratory SOPs. For samples where field or laboratory comments note visible contamination, the level-code assignment is based on an outlier test that compares the chemical concentrations of the sample to the historical record of concentrations at the individual site. Level codes are also assigned on the basis of the data QA specialist's review of FORFs, rain gage charts, the CAL-site correspondence, site visitation information, and information furnished by the CAL site liaison. Rules for level codes are given in the document cited in the previous section (Dossett, 1990) and in Operational Procedures for the Final Review of NADP/NTN Data by the CAL Quality Control Officer (Morden-Moore and Bowersox, 1989). Computer programs used in the validation process are documented in Dzurisin and Bowersox (1989). After this review, the FORFs and a data file containing the most current merged and coded field and chemical-analysis data are sent to the Coordination Office. Other data files sent to the Coordination Office contain updated records of previously sent, CAL-validated, merged data, and a listing of samples that were assigned either a protocol or level code, including the reason for each validation code assignment.

Final validation of merged data takes place at the Coordination Office under the direction of the NADP/NTN data base manager. The data transferred to the Coordination Office are validated using data validation rules maintained in a special computer file at the Coordination Office. These rules use the CAL level- and protocol-codes, but group the samples into less specific categories. The procedures are described in Scott and Reuss (1989a).

4.5.5 External Audit Information

The NADP/NTN data base manager receives notification of audit schedules and tracks site participation. This tracking record and the audit results become a permanent portion of the network data. The QA manager verifies and validates external audit information by requesting a summary report of the audit from the auditing agency. These reports may be preliminary or final. Using the audit results entered into the data management system at the Coordination Office and the tracking records, the QA manager attempts to duplicate selected summary tables, published in the various reports. Discrepancies are resolved with the appropriate agency.

4.6 RECORD KEEPING

4.6.1 Network Data

Forms that originate at field sites (FORFs and rain gage charts) are archived at the Coordination Office except as noted in Section 2.6. Other site records that originate at the CAL, such as transcripts of communications and other correspondence, are attached to the second of the three-part FORF and archived at the CAL. Results of analytical measurements including original paper records and quality assurance results from instrumentation that are filed by the analysts and the laboratory quality assurance specialist are also archived at the CAL.

Computerized data records are maintained in a DBMS or in computer files at both the CAL and Coordination Office. Data files containing merged and validated field data, chemical analysis results and screening codes are sent to the Coordination Office where they are archived.

Data files received from the CAL are copied to a master tape(s) and stored along with the FORFs and rain gage charts. The data base portion of network data resides in a DBMS on the POA and MELICA nodes of the SUN 3 UNIX network at the Natural Resource Ecology Laboratory (NREL) at Colorado State University.

Records stored at both the CAL and Coordination Office are stored for the life of the project. At the CAL both paper and electronic records are kept under the supervision of the CAL director. At the Coordination Office paper records are maintained under the supervision of the associate coordinator and electronic records are maintained under the direction of the QA Manager.

4.6.2 Updating Network Data

Network data are updated only with the concurrence of the data group that is responsible for the original data. Data records are updated when the information has passed all appropriate verification and validation steps outlined in this Quality Assurance Plan.

Full documentation of changes to network data is outside the resources of the monitoring program. Therefore, the documentation of updates to network data are limited to replacing old data with the most current information and providing, on a record basis, the date of the most recent change to the entire record. Individual data-field time-stamped changes are not supported. The QA manager monitors the frequency of record updates in network data.

4.7 QUALITY CONTROL

4.7.1 Data Collection, Entry, Transfer, and Transformation

Each manual entry of field and chemical analysis data into computer files is made twice on separate occasions and compared to ensure accurate data entry. If differences are found, the data are manually checked and corrected.

An error checking protocol is employed for data files transferred directly by computer or by data tape or disk. For tape or disk transfer, 5 percent of the records are transferred by an alternate route, such as electronic mail or hardcopy documentation. The alternate records are compared to the tape records, and, if errors are found, the entire data set is repassed. For direct transfers, system error-checking utilities (checksums) are used, such as in KERMIT, FTP, etc.

Data transformations are checked manually for correctness and to ensure that they meet the data verification objectives outlined in Section 4.3.2 for each new application. Applications include new programs, new reports, and new computer systems and software.

4.7.2 Data Verification and Validation

Every month, the CAL sends each site a computer generated printout of the information supplied on the FORF, along with computer generated messages concerning errors or potential problems at the site. A separate page contains preliminary ion concentration data. Site operators are asked to respond to any deficiencies noted on the printouts and to verify the FORF information contained therein (also see Section 4.11.1).

At the CAL, assigned data validation codes (protocol and level codes) are reviewed monthly by reviewing the coding of 10-20 randomly selected samples with the people responsible for assigning codes.

At the Coordination Office a 25 percent random subset of each batch of weekly FORFs received from the CAL is rekeyed and loaded into a separate computer file. Information common to the FORF and data tape is compared by computer programs to identify inconsistent entries. Discrepant entries are reviewed to ensure that adequate documentation is available to support the data-tape entries. Additionally 5 percent of the data tape records that have been invalidated during the data validation process are compared to original data sources. Unsubstantiated, erroneous, or otherwise ambiguously coded samples are returned to the CAL for clarification.

4.8 PERFORMANCE AND SYSTEM AUDITS

The Subcommittee on Data Management and Analysis conducts a system audit of the network data management groups biennially (every two years). Results of the audit are reported to the Quality Assurance Steering Committee and to the QA manager. The reports are made available in the QA manager's annual quality assurance report.

4.9 PREVENTIVE MAINTENANCE/SERVICE

At the CAL, a system of regular deliberate duplication of computer files on magnetic tapes and diskettes is used to maintain and prevent loss of records. The NADP/NTN database plus the programs and procedures used to introduce, access, edit, summarize, and report data that is stored in the database, are maintained on a VAX 11-780 computer. Tape backups of the user disk pack, where these files are stored, are made on the following schedule:

1. week days for all files that have been changed since the previous backup (daily backups are kept for one week); and

2. every Friday (or the nearest work day) for all files old, new, changed, and unchanged (weekly backups are kept for one month and the last one of the month is kept for three months).

Backups of VAX files are the responsibility of the ISWS computer system operator. The system operator also oversees a maintenance agreement covering the VAX computer, the disk drive, and communications hardware, and maintains the software that supports system-wide communications, including electronic mail. Backups of files kept on personal computers are the responsibility of each personal computer operator. These backups consist of files copied to diskettes from internal personal computer magnetic disks. Commercial software used on the personal computers is updated as needed, and bug reports and work-arounds supplied by the vendors are implemented as necessary.

At the Coordination Office, preventive maintenance consists of daily tape back-ups of all computer disks by the UNIX systems manager at the Natural Resource Ecology Laboratory and the implementation of bug reports and work-arounds provided by software and hardware vendors. Support for general computer services, including LAN (local area network) support, operating system support, and general common use software support, is maintained through the services of the UNIX systems manager. Project specific software, such as the DBMS software, is maintained through a service/support contract with the software vendor. Computer hardware used for the storage and processing of NADP/NTN data are maintained through a service contract with the hardware vendors.

4.10 CORRECTIVE ACTION

Corrective action in data management activities follows the general Remedial Action Plan outlined in Section 1.5. If an error is found during data processing or if any record fails a QC test, the reason is determined with the help of the appropriate, responsible person who originated the data. If appropriate, corrections are made to the network data and/or primary data files and documents. A notification of change is sent to the other data group (Figure 4.1) if the change has an impact on previously finalized data.

4.11 DATA REPORTING AND DOCUMENTATION

4.11.1 CAL Preliminary Data Reports

The CAL sends the site operator and supervisor a 2-page computerized report that contains preliminary results of the CAL's chemical analysis and a computerized version of the information contained on the FORF. The reports are received approximately six weeks after a site begins operation and monthly thereafter. Site operators and their supervisors are expected to review and verify the information in the reports and to respond to the computer-generated messages, as necessary. Any other information regarding data quality resulting from this review is forwarded to the CAL. Responses are made by annotating the appropriate report page and mailing it back to the CAL in the shipping container during the next regularly scheduled sample submission. The formats of these reports are detailed in Bigelow and Dossett (1988).

4.11.2 Reports of Weekly Data

Site operators and supervisors receive a final report of their site's validated, quality-coded field and chemistry data. The report also includes a listing of the agencies that supported the site financially during the reporting period and the results of the site's participation in external quality assurance programs. Data contained in the report are also available on 9-track, 1600 bpi, ASCII-formatted tape.

Specific procedures and computer programs used at the Coordination Office to produce this data report are documented in a single location on the computer network located at the Coordination Office. The use of these files and programs are given in Procedures Manual: NADP/NTN Semiannual Data Report (Scott and Reuss, 1989b). The reports and their formats are specified by the Technical Committee.

4.11.3 Annual Data Reports

The annual data report summarizes the chemistry of precipitation samples collected at sites in the NADP/NTN monitoring network. The main body of the report contains annual and seasonal statistical summaries of the weekly precipitation chemistry data for a reporting year. Corresponding weekly data along with data quality coding that supports the annual and seasonal summaries are also given. Geographical distributions of selected ionic constituents of precipitation are illustrated by isopleth maps.

Specific procedures and computer programs used at the Coordination Office to produce this report are documented in ASCII files located in a single directory on the computer network at the Coordination Office. The content and format of the report is specified by the Technical Committee.

4.11.4 User-Requested Data Reports

Semiannually, the Coordination Office transfers an exact duplicate of network data to the Acid Deposition System (ADS), an EPA-sponsored data base for statistical reporting of North American atmospheric-deposition data (Watson and Olsen, 1984), located at Battelle's Pacific Northwest Laboratory in Richland, WA. This facility has privileged access to all network data and additionally serves as a back-up for the network data base. In addition to the ADS data transfer, other custom requests are honored whenever possible.

4.11.5 Changes in Previously Reported Network Data

The routine reporting of changes to previously distributed network data is usually limited to the ADS data system. However, users of data tapes can, on request, receive updates at regular intervals. Those who do request updates receive an extra data file that contains the most current contents of any previously distributed data record that have changed since the user made their last request. Only entire records are revised and redistributed. The network does not account for changes in individual data fields within each record. Records are defined by the schema of the DBMS. A summary of the number of changes made to data records is included in the QA manager's annual QA reports.

4.11.6 Quality Assurance Reporting

At least quarterly, the laboratory and data QA specialists and the laboratory manager notify the CAL director of any changes in the chemical analysis of samples or data management activities at the CAL. This notification may be formal or informal and includes information concerning any changes in chemical analysis, data verification or validation procedures, and any changes in site liaison policy. Laboratory QA summaries, data completeness summaries, problem documentation, and associated corrective actions taken during the period may also be included as a part of this notification. All of the above items, along with a formal QA report of laboratory operations, are submitted annually to the QA manager. The QA manager issues an annual quality assurance report for the entire network operation. The report includes separate sections detailing site operations, laboratory operations, and data handling, and it addresses each of the objectives presented in this Quality Assurance Plan.

4.11.7 Information Repository

The following information, consisting of computer records stored in files or within a DBMS, hardcopy reports, and records are placed in a data repository in the Coordination Office.

1. Site Description Questionnaires
2. Field Observer Report Forms (FORFs)
3. Rain gage charts
4. Chemical analysis results
5. Data-quality coding recommendations
6. External audit records
7. Miscellaneous standard forms described in SOPs
8. Quarterly, semiannual, and annual reports and summaries of precipitation chemistry
9. Quality Assurance Reports
10. External Audit Reports
11. SOP documentation listed in this plan

SECTION 5
OVERALL ASSESSMENT OF NETWORK QUALITY

5.1 DESCRIPTION

Previous sections of this Quality Assurance Plan address separately the quality of Field Operations, Laboratory Operations, and Data Management Operations. An overall assessment of network quality, however, requires that these separate estimates be integrated, or that programs be established to make the overall quality estimate using an 'end-of-the-pipeline' approach. In the NADP/NTN monitoring program, a combination of these approaches is utilized to assist users of NADP/NTN data in establishing overall network data quality.

To facilitate the evaluation of network data quality within the program and by others, the monitoring program maintains five descriptors of overall data quality: completeness, precision, accuracy, comparability, and representativeness. These descriptors are the basis for reporting the overall data quality of the monitoring program. Estimates of the data quality are made for the weekly values and for the seasonal and monthly aggregates. Regional estimates are also made using the same techniques but using the ecoregion as the regional discriminator. The network reports weekly concentration and deposition values for the analytes listed in Table 5-1. Quality estimates are also made for collector bucket volumes, rain gage volumes, and individual monitoring site locations.

Table 5-1

Analytes For Which Data Quality Are Defined

pH	Specific conductance
Calcium	Magnesium
Sodium	Potassium
Ammonium	Nitrate
Sulfate	Chloride
Ortho-phosphate	

5.2 ORGANIZATION AND RESPONSIBILITY

Responsibility for the assessment of network data quality is shared by the various federal agencies and other public and private organizations that support the network's component operations. Responsibility for coordinating the assessments and for reporting values for the five quality descriptors resides with the QA manager.

5.3 OBJECTIVES AND GOALS

The objectives and goals of the overall assessment of network quality are to establish scientifically acceptable estimates of the completeness, precision, bias, comparability, and representativeness of NADP/NTN monitoring data.

5.4 COMPLETENESS

An assessment of the completeness of network data is made by comparing the number of observations and measurements made by the network, on an annual basis, to the number of observations and measurements that were planned to be made by the network during an annual period. For the overall assessment of completeness these comparisons are limited to annual tallies of the number of chemical analyses made, the number of rainfall measurements made, and the number of monitoring locations for which data have been obtained. Additionally, because the network is committed to spatial and temporal aggregation of its data, selected spatial and temporal comparisons are also made.

5.4.1 Analytes

The completeness of the network's chemical analysis measurements is reported annually as the percentage of samples with a complete set of chemistry values. To provide additional information for network management, these percentages are reported both by site and by laboratory type code (See Tables 3-2 and 3-3). The tallies also include the percentage of missing samples and the percentage of samples whose values were determined to be below analytical reporting limits. Field chemistry percentages are reported separately from laboratory percentages.

5.4.2 Bucket and Rain Gage Volumes

The percentage of annual samples with reported bucket and rain gage volumes is used to assess the completeness of the rainfall measurements made by the network. Also included in the assessment is the percentage of samples where bucket volume is the only measure of rainfall. The percentage of days that are represented by complete rainfall records is also reported. As in the previous section, the information is reported both by laboratory type code and by site.

5.4.3 Monitoring Sites

Changes in the number and locations of sites on an annual basis are used to describe how the completeness of the network's sampling coverage is changing. Summaries of both the number of operating and closed sites are presented as well as a distribution showing the number of months that sites have been active in the network. Additionally, the completeness of data at individual monitoring sites is reported annually in accordance with the goals listed in Section 4.3.

5.4.4 Seasonal and Regional Estimates

Overall seasonal and regional estimates of completeness are made using the goals described in Section 4.3.1. Estimates are made for each season for the entire network, each region for the entire year, and each season-region combination. Calculated values include the following:

1. Average percentage of the days per site where precipitation estimates are available.
2. Average percentage of the days per site where valid samples are present.
3. Average percentage of the volume per site represented by valid samples.

5.5 PRECISION

Overall network precision is derived from paired collocated sampling equipment. Collocated data allows the precision of analyte measurements and rainfall amounts to be calculated for individual samples (weeks) as well as for longer averaging times. Equipment is considered to be collocated only if the additional sampling devices are within 30 m of existing NADP/NTN monitors and are serviced by the same site operator.

5.5.1 Seasonal and Regional Estimates

Ecoregion, seasonal, and individual sampler precision estimates are made by statistically pooling the variances of the collocated equipment consistent with the aggregation desired. Additionally, the variance between sites can be estimated using an analysis of variance model with random nested effects.

5.5.2 Field Chemistry

The network has not established precision estimates for field chemistry measurements.

5.5.3 Monitoring Sites

Precision estimates for individual monitoring sites are not completed routinely. Estimates are only made if a site is equipped with a collocated sampling device.

5.6 ACCURACY

Accuracy or, more appropriately bias, is difficult to assess on an overall basis because there is no standard network that the performance can be measured against. Bias can be estimated, however, by comparing NADP/NTN data to those from other similar networks where NADP/NTN sampling equipment is collocated. This type of comparison identifies systematic differences between the two networks. If collocated equipment precision is known, then overall network measurement error attributable to the network's monitoring technique can be estimated as the sum of the random and systematic error. This type of collocated study follows, in part, the general framework of collaborative testing outlined by Youden (1967).

5.6.1 Chemical Analyses and Rain Gage Volumes

In lieu of a standard network, accuracy is inferred from pooled estimates of bias between a number of networks operating at a single site. The assumptions and calculations of this collaborative test are well defined by Youden (1967). The efficiency of the accuracy estimate is proportional to the number of networks and sites participating, and the estimate is further dependent on the amount of missing data and assumptions of Gaussian distributions of sampled populations that have, in some cases, been shown not to be true (Topol et al., [1982; 1985]). In spite of these weaknesses, collaborative testing techniques are an effective means of estimating bias without requiring the development of new field sampling programs. These techniques have the further advantage of producing data that may be easily reassessed if new nonparametric statistical techniques are developed to handle or quantify the degree of departure of the data exhibit from more normalized distributions.

Like the precision computation, accuracy estimates are made using collocated stations that are no more than 30 m apart. If a sufficient number of stations are not collocated with other networks, then stations that are more than 30 m apart (but within the same ecoregion) are considered in order to increase the number of stations that are available for computing accuracy estimates.

An overall accuracy estimate is assigned to network data by computing a median bias estimate from a number of network comparisons. The departure from the median value plus the network precision value is the presumed accuracy of the network data.

5.6.2 Bucket Volumes and Rain Gage Amounts

Bias in bucket volumes is determined by computing the average catch of the weekly wet-deposition bucket volume in relation to the standard rain gage used by the network. Distributions of the differences document regional, seasonal, and monitoring site bias.

Accuracy of network standard rain gage values is determined by comparing annual network standard rain values to nearby National Weather Service (NWS) gage values. NWS stations are considered to be nearby when the station is within 10 km of a monitoring station and within a 200 m elevation (Bigelow, 1986). On a regional and seasonal basis, the degree of departure from the NWS gage amounts is assumed to demonstrate bias. This comparison assumes the correctness of NWS gage amounts.

Daily precipitation amounts will also be classified by precipitation type to show the distribution of types by site and ecoregion.

5.6.3 Monitoring Site

Because there is no standard site, bias at a monitoring site is directly related to representativeness assumptions. The NADP/NTN monitoring program relies on comparability estimators (Section 5.7) and representativeness estimators (Section 5.8) as indicators of monitoring-site bias.

5.7 COMPARABILITY

The comparability of network data over time is one of the foremost goals of the monitoring program. Values and measurements obtained in one year should be comparable to values and measurements produced in another. This also holds for monitoring locations to ensure that results from one location can be compared with confidence to another. Because the network has chosen spatial and temporal goals for data reporting, both types of comparisons are made.

5.7.1 Spatial Integrity

Principal-component analysis or another type of clustering analysis is used annually to establish anomalous sites in ecoregion groupings; these anomalous sites are identified. Attempts are made to explain the anomaly.

5.7.2 Temporal Integrity

Time-series plots and decompositions (Cleveland et al 1981; Becker and Chambers, 1984) for the period of each site are examined on an annual basis for anomalous behavior. Anomalous data are identified, and attempts are made to explain the reason for the anomaly. Comparability is verified by ensuring that there are no quality assurance anomalies in the temporal record created for each site.

5.8 REPRESENTATIVENESS

The representativeness of NADP/NTN monitoring data can only be established when the specific goals for its use are known. Therefore the network can only offer indicators of representativeness which it feels are useful in helping others establish the representativeness of network data to their specific study or assessment. Because the network cannot anticipate all uses of its data, representativeness descriptors reported by the network are limited. Spatial representativeness is addressed primarily through the use of the ecoregion classification of sites after Bailey (1978; 1980) and Bailey and Cushwa (1981). Temporal representativeness is expressed by grouping data by meteorological seasons (Trenbeth, 1983), calendar months, and annual calendar years. Representativeness estimates reported by the network include precipitation type (rain, snow, mixed), volumes for samplers and rain gages, and source emissions (SO_x, NO_x) for monitoring sites. Data users are encouraged to make other groupings to evaluate the representativeness of NADP/NTN data in meeting their data quality objectives.

5.8.1 Combinations of Chemistry and Volume Including Deposition

On a seasonal and regional basis, the representativeness of both chemistry and rain gage amounts is estimated by determining the number of samples that are classified into each of the four laboratory type codes (W, WA, T, DA) and three note code (NS, BU, and Time Limit) categories used to process and quality code weekly data (see Bigelow, 1986). Because laboratory types are based on sample volumes, counts of these categories form a distribution of precipitation amounts for a given site, season, or ecoregion. Note code counts also reveal a distribution of sample validity by site, season, and ecoregion. A second estimate of representativeness is obtained by calculating the amount of volume and deposition in each lab type and note code category. A third estimate of representativeness is made by examining the data distributions and sample validity statistics presented on a by-site basis in the annual summaries of site and laboratory data published by the monitoring program.

The representativeness of monitoring locations is still the subject of much debate. In lieu of a more definitive site representativeness classification, the Unified Deposition Data Base Committee's (UDDC) Site Representativeness Rating is used to report the representativeness of sites (Olsen et al 1990). Both the rating and the results of each evaluated key parameter are presented. Evaluation of each key parameter is based upon NADP/NTN Site Visitation Program results, and on the most current emission inventory available to the NADP/NTN Coordination Office. The frequency of updating the monitoring site representativeness rating is directly tied to the frequency of site visits.

5.9 REPORTING AND DOCUMENTATION

Reports of overall assessments of the monitoring program are submitted as a report or recommendation to the appropriate subcommittee. Recommendations for corrective action are discussed and authorized by the subcommittee and the Technical or Executive Committee in accordance with the Remedial Action Plan.

GLOSSARY

accuracy -- the degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random (precision) and systematic error (bias).

aliquot -- a representative portion of the whole.

analyte -- the substance, in a chemical analysis, whose concentration is to be measured.

audit -- a systematic evaluation to determine the operational quality of some managerial or operational function or activity.

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

blank sample -- a clean sample or a sample of matrix processed so as to measure artifacts in the measurement (sampling and analysis) process.

blind sample -- a subsample submitted for analysis with a composition and identity known to the submitter but unknown to the analyst and used to test the analyst's or laboratory's proficiency in the execution of the measurement process.

bulk sample -- a wet-side sample that has been exposed continuously to both wet and dry deposition for the entire sampling period.

certified value -- the reported numerical quantity that appears on a certificate for a property of a reference material.

collocated sampler -- an additional sampling device(s) located within 30 meters of the primary sampling device and that is used to supply replicate samples for estimating precision and assessing bias and comparability.

comparability -- a measure of the degree to which methods, data sets, and decisions can be represented as similar.

completeness -- the amount of valid data obtained compared to the planned amount (i.e., sample size) usually expressed as a percentage.

dry deposition -- all forms of deposition derived from the net vertical transfer of chemical species to a surface that are not the result of precipitation. Dry deposition processes include both turbulent diffusion and gravitational settling. Dew and frost are anomalous forms of dry deposition which rely upon a near surface, condensation process as their principle means of effecting the net vertical transfer.

duplicate -- consisting of or existing in two identical or corresponding examples, such as a duplicate sample or analysis.

ecosystem -- any level in an ecological hierarchy defined as an interconnected system of parts.

method detection limit (MDL) -- the minimum concentration of an analyte that can be reported with 99 percent confidence that the value is above zero.

precision -- the degree of agreement of repeated measurements of a homogenous sample by a specific procedure, expressed in terms of dispersion of the values obtained about the mean value. It is often reported as the sample standard deviation.

quality assurance (QA) -- an integrated system of activities involving planning, quality control, reporting, and remedial action to ensure that a product or service meets defined standards of quality.

quality control (QC) -- the overall system of technical activities whose purpose is to measure and control the quality of a product or service so that it meets the needs of the users. The aim is to provide quality that is satisfactory, adequate, dependable, and economical.

reference material -- a material, one or more properties of which are sufficiently well established to be used for the calibration of an apparatus, for the assessment of a measurement method, or for assigning values to materials.

replicate measurement -- the measurement of the variable of interest performed on more than two representative subsamples. Replicate analysis is used to assess variance.

representativeness -- the degree to which data accurately and precisely represent the frequency distribution of a characteristic in the population.

spike -- a known mass of target analyte added to a sample or subsample; used to determine recovery efficiency or other quality control purpose.

splits -- two or more aliquots of the same sample treated identically throughout the laboratory analytical procedure. Analyses of laboratory split samples are beneficial when assessing precision associated with laboratory procedures but not with collection and handling.

standard operating procedure (SOP) -- a written document that details the method of an operation, analysis, or action whose techniques and procedures are thoroughly prescribed and that is accepted as the method for performing certain routine or repetitive tasks.

validation -- the process by which a sample, measurement method, or unit is systematically determined to meet specified performance criteria.

BIBLIOGRAPHY

American Society for Testing and Materials. (Always most recent year). *Annual Book of ASTM Standards, Vol. 14.02.* American Society for Testing and Materials, Philadelphia, PA.

Bailey, R.G. 1978. Description of the Ecoregions of the United States. U.S. Forest Service Intermountain Region, Ogden, UT.

Bailey, R.G. 1980. Description of the Ecoregions of the United States. Miscellaneous Publication 1391. U.S. Department of Agriculture.

Bailey, R.G., and C.T. Cushwa. 1981. Ecoregions of North America After the Classification of J. M. Crowley. Scale 1:12,000,000. U.S. Fish and Wildlife Service, Eastern Energy and Land Use Team, Kearneysville, WV.

Becker, R.A. and J.M. Chambers. 1984. *S: An Interactive Environment For Data Analysis and Graphics.* Wadsworth, Inc., Belmont, CA.

Bigelow, D.S. 1984. Instruction Manual for NADP/NTN Site Selection and Installation. National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO.

Bigelow, D.S. 1986. Quality Assurance Report: NADP/NTN Deposition Monitoring, Field Operations, 1978 through 1983. National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO.

Bigelow, D.S. 1988. Quality Assurance Support for the National Atmospheric Deposition Program and National Trends Network Monitoring Activities: 1984-1987. Environmental Monitoring Systems Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC. EPA/600/4-88/004.

Bigelow, D.S. and S.R. Dossett. 1988. Instruction Manual for NADP/NTN Site Operation. National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO.

Bowersox, V.C. 1985. "Data Validation Procedures for Wet Deposition Samples at the Central Analytical Laboratory of the National Atmospheric Deposition Program." In *Transactions of the APCA/ASQC Specialty Conference on Quality Assurance in Air Pollution Measurements, TR-3,* Boulder, CO, APCA, Pittsburgh, PA. October 1985.

Cleveland, W.S., S.J. Devlin, and I.J. Terpenning. 1981. "The SABL Statistical and Graphical Methods and the Details of the SABL Transformation, Decomposition and Calendar Methods." Bell Laboratory Memorandum, Bell Laboratories.

Daum, K.A., C.A. Salmons, R.C. Shores, and W.C. Eaton. 1988. Quality Assurance Project Plan for Systems and Performance Audits of Acid Precipitation Collection Sites--NADP/NTN and SON Networks. Report prepared under contract for the U.S. Environmental Protection Agency, Research Triangle Institute, Research Triangle Park, NC. RTI/4031/00-01D.

Dossett, S.R. 1990. Operational Procedures for the Initial Review of NADP/NTN Wet Bucket Data by the CAL Site Liaison (draft document). Illinois State Water Survey, University of Illinois, Champaign, IL.

Douglas, K.E., and V.C. Bowersox. 1989. Operational Procedures for the Management of the NADP/NTN/CAL Data Bases by the CAL Data Base Manager (draft document). Illinois State Water Survey, University of Illinois, Champaign, IL.

Douglas, K.E., S. Bachman, V.C. Bowersox, B. Demir, S.R. Dossett, K.O. James, A.L. Morden-Moore, M.E. Peden, and J. Sauer. 1989. Operational Procedures for the CAL Field Operations Course for NADP/NTN Site Personnel (draft document). Illinois State Water Survey, Champaign, IL.

Dzurisin, G. and V.C. Bowersox. 1990. Computer Hardware and Programs, Procedures and Software Used by the NADP/NTN/CAL Data Management Group (draft document). Illinois State Water Survey, University of Illinois, Champaign, IL.

Every Tuesday Morning. 1989. Produced by the U.S. Geological Survey, U.S. Geological Survey, Office of Acidic Deposition, Reston, VA (video).

Franson, M.A. (ed). 1985. *Standard Methods for the Examination of Water and Wastewater.* 16th Edition, American Public Health Association, Washington, DC.

Lusis, M.A., W.H. Chan, E.C. Voldner, R.J. Vet, A.R. Olsen, D.S. Bigelow, and T.L. Clark. 1986. "A Unified Wet Deposition Data Base for Eastern North America: Data Screening, Calculation Procedures, and Results." Paper No. 86-29.1. Paper presented at the 79th Annual Meeting of the Air Pollution Control Association, Minneapolis, MN, June 1986.

Morden-Moore, A.L. 1989. Operational Procedures for the Receipt and Check-In of NADP/NTN Samples by the CAL (draft document). Illinois State Water Survey, University of Illinois, Champaign, IL.

Morden-Moore, A.L. 1990. Operational Procedures for the Computer Entry of Field Observer Report Form (FORF) Data, Chemical Analytical Data, and Descriptive Information of the CAL of the NADP/NTN (draft document) Illinois State Water Survey, University of Illinois, Champaign, IL.

Morden-Moore, A.L., and V.C. Bowersox. 1989. Operational Procedures for the Final Review of NADP/NTN Data by the CAL Quality Control Officer (draft document). Illinois State Water Survey, University of Illinois, Champaign, IL.

Olsen, A.R., Voldner, E.C., Bigelow, D.S., Chan, W.H., Clark, T.L., Lusis, M.A., Misa, P.K. and R.J. Vet. 1990. "Unified Wet Deposition Data Summaries for North America: Data Summary Procedures and Results for 1980-1986." Atmos. Environ. 24A(3) pp. 661-672.

Olsson, C. and S. Reuss. 1989. Procedures for Processing of NADP/NTN Site Visitation Information (draft document). National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO.

Olsson, C., S. Reuss, and C. Simmons. 1990. Procedures Manual: Coordination Office Equipment Depot (COED), Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO.

Peden, M.E., S.R. Bachman, C.J. Brennan, B. Demir, K.O. James, B.W. Kaiser, J.M. Lockard, J.E. Rothert, J. Saur, L.M. Skowron, and M.J. Slater. 1986. Development of Standard Methods for the Collection and Analysis of Precipitation. Illinois State Water Survey, University of Illinois, Champaign, IL, 375 pp. Illinois State Water Survey Contract Report 381.

Reuss, S. 1989a. Procedures Manual: Intersite Comparison Program (draft document). National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Ft. Collins, CO.

Reuss, S. 1989b. Procedures Manual: NADP/NTN Blind Audit Program (draft document). National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO.

Reuss, S., D.S. Bigelow, C. Simmons, S. Molden, and G.R. Scott. 1990. Procedures Manual: Evaluating and Documenting NADP and NTN Monitoring Sites. National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO.

Robertson, J.K. and J.W. Wilson. 1985. Design of the National trends Network for Monitoring the Chemistry of Atmospheric Precipitation, United States Government Printing Office, Washington, DC. U.S. Geological Survey Circular 964.

Scott, G.S. and S. Reuss. 1989a. Procedures Manual: Weekly Data Processing (draft document). National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO.

Scott, G.S. and S. Reuss. 1989b. Procedures Manual: NADP/NTN Semiannual Data Report (draft document). National Atmospheric Deposition Program, Natural Resource Ecology Laboratory, Colorado State University, Fort Collins, CO.

See, R.B., Willoughby, T.C., and M.H. Brooks. 1989. Programs and Analytical Methods for the U.S. Geological Survey Acid Rain Quality Assurance Project. Water Resources Investigations Report. U.S. Geological Survey, Denver, CO.

Stensland, G.J., M.E. Peden, and V.C. Bowersox. 1983. "NADP Quality Control Procedures for Wet Deposition Sample Collection and Field Measurements." 76th Annual APCA Meeting, Atlanta, GA. June 1983. Paper No. 83-32.2.

Topol, L.E., G. Colovos, and R. Schwall. 1982. "Precision of Precipitation Chemistry Measurements." Proceedings of the Air Pollution Control Association Specialty Conference on Acid Precipitation, Detroit, MI, November 1982.

Topol, L.E., M. Lev-On, J. Flanagan, R.J. Schwall, and A.E. Jackson. 1985. Quality Assurance Manual for Precipitation Measurement Systems. Environmental Monitoring Systems Laboratory, Office of Research and Development, U. S. Environmental Protection Agency, Research Triangle Park, NC.

Trembeth, K.E.. 1983. "What are the Seasons?" Bull. Amer. Meteorol. Soc. 64:1276-1282.

Unified Deposition Data Base Committee. 1986. A Unified Wet Deposition Data Base for Eastern North America: Data Screening, Calculation Procedures, and Results for Sulphates and Nitrates. Report to the Canadian Federal-Provincial Research and Monitoring Co-Ordinating Committee. Ontario Ministry of the Environment, 880 Bay Street, Toronto, Canada.

United States Department of Agriculture. 1977. Manual for Cooperative Regional Research, Cooperative State Research Service, Washington D.C.

Watson, C.R., and A.R. Olsen. 1984. Acid Deposition System (ADS) for Statistical Reporting: System Design and User's Code Manual (with appendices). U.S. Environmental Protection Agency, Research Triangle Park, NC, 32 pp. EPA 600/8-84-023.

Weast, R.C. (ed). 1989. *CRC Handbook of Chemistry and Physics,* 70th edition, CRC Press, Inc., Boca Raton, FL.

Youden, W.J. 1967. *Statistical Techniques for Collaborative Tests.* The Association of Official Analytical Chemists, Washington, DC, 64 pp.