QUALITY ASSURANCE PLAN
Mercury Deposition Network

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NATIONAL ATMOSPHERIC DEPOSITION PROGRAM

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The NADP is developing a revised Network Quality Assurance Plan. This Mercury Deposition Network Quality Assurance Plan will be superseded by the Network Quality Assurance Plan when it is released in 2005. Further information is available from the NADP Program Office.

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OVERVIEW OF QUALITY ASSURANCE PROGRAM

1.1 INTRODUCTION

This document is the Quality Assurance Plan (QAP) for all network operations of the Mercury Deposition Network (MDN). The plan is modeled after the QAP for the National Atmospheric Deposition Program and National Trends Network (NADP/NTN) (Aubertin et al. 1991). This QAP describes the Quality Assurance (QA) practices for: (a) the operation of the field sites (Section 2); (b) the operation of the Mercury Analytical Laboratory (HAL) (Section 3); and (c) the documentation, validation, error assessment, archiving, and dissemination of data (Section 4).

1.2 DESCRIPTION OF THE MDN

The objective of the Mercury Deposition Network (MDN) is to develop a regional database on the weekly concentration of total mercury in precipitation and the seasonal and annual flux of total mercury in wet deposition. Once established, the MDN may expand to include additional analyses for methyl mercury in wet deposition. The data will be used to develop an information base on spatial and seasonal trends in mercury deposited to surface waters, forested watersheds, and other sensitive receptors.

MDN became a subnetwork within the NADP/NTN in January 1996. A transitional network of 13 sites operated during 1995 and the network will grow to over 30 sites across North America. MDN addresses the importance of Hg deposition to natural ecosystems, human health, and precipitation quality with the collection, quality assurance, and publication of data on total mercury in wet deposition. It is clear that a special collector must be used to preserve the integrity of the sample. The MDN collector is a modified Aerochem Metrics wet/dry collector with two sampling trains under the wet-side lid. One of acid cleaned and baked glass for Hg collection, and one that could be made compatible for the future collection of other trace metals and organics.

Recent research on the global mercury cycle has shown that this pollutant is ubiquitous, and is transported far from its initial sources prior to deposition. The methyl mercury levels in fish of pristine lakes around the world are found to be high. Therefore, one of the goals of the MDN is to

collect the data necessary to allow evaluation of the spatial and temporal variability in the wet deposition of Hg. The MDN will obtain regional total Hg measurements in precipitation to obtain reliable and accurate data over time and space.

Several groups have unique roles in producing MDN data, including state and federal site sponsors, the Hg Analytical Laboratory (HAL), and the NADP Program Office. According to protocols, sites use standardized instrumentation and procedures to make field measurements and to collect weekly wet deposition samples. The samples are sent to the HAL, where all samples are analyzed according to documented procedures. The data obtained from the sites and from the HAL are combined into a database and distributed to all sites and to the public upon request. Annual summaries and reports are also made available through the NADP Program Office.

1.3 ORGANIZATION AND RESPONSIBILITIES

1.3.1 Organization of MDN

The MDN is a cooperative effort of the NADP Program Office, the NADP Technical Committees, the MDN advocates, and the HAL. In its general structure the MDN follows the organization of the NADP as outlined in their Quality Assurance Plan. The MDN therefore will follow the guidelines established for interregional research projects by the Cooperative State Research Service (USDA, 1986).

The responsibilities of the NADP Technical Committee, Executive Committee, Budget Advisory Committee, and the Subcommittees will be the same for the MDN as they are for NADP. Workgroups within each of the NADP subcommittees will be set up to address specific MDN issues during the first years of its development.

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 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, 1986). 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, and the chairman of each of the three subcommittees. Sitting on this committee as advisors are the State Agricultural Experiment Stations' (SAES) regional administrative advisors, the CSREES representative, the USGS representative, the director of the CAL, the program coordinator, and the NAPAP representative. A MDN representative also attends the Executive Committee Meetings.

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

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, representatives of the primary funding agencies for the network, and a MDN representative, meets annually to review program expenditures and to plan for future funding. The committee is co-chaired by the USGS representative and the program chairman of the NADP Technical Committee.

1.3.1.4 Program Office

The staff at the NADP Program Office at Illinois State Water Survey are responsible for administering the monitoring program on a daily basis. Primary responsibilities of the NADP staff include budget and funds management, data management, data reports, and quality assurance. Specifically the Program Office will supply replacement parts for the modified Aerochem Metrics

collector (i.e. motor boxes, sensors, lid seals, rain gauge clocks, and event recorders) through the Network Equipment Depot (NED); disseminate the preliminary data to sites, supply data requests to the public, and report the total mercury annual, seasonal, and monthly values in the annual NADP data summary report; contract the HAL for analytical services and the sites for analytical costs; coordinate with cooperating agencies and other programs; and perform other activities that enable the network to perform smoothly.

1.3.1.5 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). MDN workgroups will be set up in each of the subcommittees to address specific MDN issues. These committees provide input into the Technical, and Executive 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.

1.3.2 Charges and Responsibilities of the Subcommittees

1.3.2.1 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 analytical laboratory concerning analytical methods, laboratory procedures, and

quality control (QC).

4. Assure that the appropriate analytical procedures are used and that appropriate QC and QA protocols are followed by periodic audits of the analytical laboratory.
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 QA Plan; when the needs of the program change, this subcommittee reviews and recommends changes in the QA 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.

1.3.2.2 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 HAL, and the Program Office. This includes the review and approval of the design of the MDN Observer Form (MOF) and the precipitation rain gauge 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 HAL, the Program Office; and all criteria for data reporting.
5. Review and approve the format of data reports and summaries from the HAL and the Program 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 HAL and Program 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 QA Plan; when the needs of the program change, this subcommittee reviews and recommends changes in the QA 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.

1.3.2.3 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 CSREES on priorities for research funding.
3. Promote communication and cooperation among effects researchers.

1.4 OBJECTIVES AND GOALS

1.4.1 Scope

Because the concentration of mercury in precipitation is so low (nano- to picomolar), 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 the minimum NADP siting criteria and use approved instruments and procedures to participate in the network. The HAL operates under a well-defined QA program with stringent QC criteria. QA continues for processing, coding, and reporting data to the Program 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 MDN QA Plan is reviewed every 3 years and revised as needed.

1.4.2 Quality Assurance Policy

Policy is formulated by the QA manager in conjunction with the MDN advocates and NADP subcommittees. 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 MDN 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 complete and concise records of network policies, procedures and quality assessments.

3. 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 MDN monitoring program, quality control is applied to all aspects of monitoring, measuring, and reporting of the total mercury deposition

values. 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 accepted calibration procedures, replicate samples, spikes, blanks, split samples, blind samples, reagent checks, system audits, 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

A site visitation program and information gathered on a site description questionnaire will address issues related to conformance of network protocols and to document the local source emissions in the vicinity of the site, near-by land-use and the site's adherence to NADP siting criteria. The condition of equipment, the performance of the site personnel, and the results of various QA tests will also be documented. Other external QA program's to monitor precision and bias of the MDN's analytical measurements need to be developed. A blind audit sample program similar to NADP's could be initiated for the MDN. Audit samples could be sent to sites randomly selected from regions in the network. An agency or laboratory (i.e., EPA or USGS) will need to be contracted to supply the blind samples to the MDN sites. At the site a portion of the sample is poured into a bottle 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 would be sent directly to the HAL in the original bottle for separate analysis. A third program provides an assessment of the comparability of the MDN's laboratory data through the HAL's participation in interlaboratory comparison programs. Collocated samplers are set up to estimate within site and overall network precision at selected MDN sites.

1.5 REMEDIAL ACTION PLAN

1.5.1 Description

The NADP Remedial Action Plan describes the sequence of actions taken to resolve problems of noncompliance with network 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.

1.5.2 Sequence of Actions

The sequence of remedial actions is based on the NADP QAP. Reports of noncompliance with program procedures, criteria, and protocols will be initially referred to the network QA manager. Possible sources of such reports are the HAL, the Program 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 will be summarized by the QA manager in semiannual reports to the NADP Subcommittees.

The QA manager will work closely with the noncomplying party in an effort to achieve compliance. In cases where compliance with program procedures, criteria or protocols cannot be achieved and where a precedent has been established for an exemption, the QA manager will recommend to the Program Office that one be granted. Moreover, the actions are documented in the site files or laboratory files. The resolution of problems involving site operations are reported to the site supervisors and sponsors by the QA manager.

1.6 REPORTING AND DOCUMENTATION

Quality assurance reports, assessments and SOPs, originating from a variety of sources will be provided to the QA manager and will be maintained in the Program Office. These documents include but are not limited to the following:

1. The MDN and NADP Quality Assurance Plans
2. The NADP Site Selection and Installation Manual
3. The Instruction Manual for MDN Site Operations
4. Analytical methods and data management procedures
5. The Mercury 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 MDN precipitation collection sites. Included in these activities are the selection and installation of monitoring locations; the collection of wet samples of atmospheric deposition; 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.

The MDN collector is designed to sample precipitation for mercury and other metals simultaneously, and is a modification of the Aerochem Metric collector (Aerochem Metrics, Inc., Bushnell, FL). Modifications include: two wet side orifices (a glass sampling train for mercury and another sampling train for the sampling of other metals or organics in the future); replacement of the aluminum lid with one of polycarbonate; Teflon-coated lid supports and Teflon-wrapped sealing foam pads; flexible sleeves at the base of the lid arms; an enclosure around the collector base; and a thermostatically controlled heater and fan to minimize temperature extremes within the enclosure and to melt snow collected in the funnels. The MDN collector was designed as part of an NADP project supported by the USGS to develop methods for measuring metals in precipitation (Vermette et al., 1994).

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. A sample change is made regardless of sample volume. The exposed sampling train (bottle, funnel and capillary tube) are removed from the sampler (the collection bottle is capped) and replaced with cleaned ones received that week from the analytical laboratory. When all required measurements have been made and all necessary observations have been recorded, the sampling train and completed standardized MDN Observer Form (MOF) are then packed for shipment and sent to the HAL by 2nd day UPS or Federal Express no later than the following day.

Equipment is maintained and checked according to standard procedures specified in a site

operation instruction manual (Welker, 1996). Replacement parts for sample collection equipment are furnished to sites on an as needed basis. Troubleshooting of all aspects of site operations is available through a site liaison at the HAL. A training video is also available for instructing site personnel in the procedures used by the network to collect, measure, and document Hg 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 liaison at the HAL.

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.). Often times 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 MDN sampling and network siting protocols are followed. Site supervisors typically review the weekly data produced at the site, assist the site operator in troubleshooting operational problems and work to make resources available to the site operator by coordinating with the agencies that cooperate to

operate the monitoring site. The site supervisor may or may not be the on-site or work supervisor of the site operator. The site supervisor may oversee operations at more than one site and is not required to be based nearby.

2.2.3 Site Operator

The site operator is the person primarily responsible for the day-to-day operation of the MDN monitoring equipment; the weekly collection, on-site measurements, and submission of precipitation samples; and sample documentation. Site operators typically perform routine maintenance and repairs on site equipment, read and interpret the rain gauge chart associated with each weekly precipitation sample, and complete and submit the weekly MOF. The site operator is also responsible for maintaining on-site records of site operations, including copies of the MOFs, rain gauge charts, and memoranda concerning site operations, and the site operations manual.

2.2.4 Site Observer

The site observer is a person designated to serve as a substitute for the site operator when the site operator is absent. The site observer is trained by the site operator or the site supervisor. More than one observer may be designated at each site. Site observer responsibilities are typically limited to the removal and replacement of the sample bottle, funnel and capillary tube, and rain gauge chart, the occasional processing of a weekly sample, and the completion of the MOF.

2.2.5 Technical Support of Collection Sites

Technical support is provided to the sites by the HAL and the Program Office. The HAL provides sites with the supplies necessary for the regular operation of each site. The HAL also provides full-time troubleshooting for operational and procedural problems via telephone or email. The Program Office provides the sites with replacement components for monitoring equipment through the NED program. The MDN coordinator provides guidance and assistance on siting and equipment. Administrative problems can be addressed to the Program Office. Each site additionally receives a training video titled Operation of the Dual-Orifice Collector (Vermette, 1994).

2.3 OBJECTIVES AND GOALS

The overall objectives of the MDN monitoring program include the estimation of data completeness, precision, bias, comparability, and representativeness. For field operations, specific goals for establishing these quality attributes are as follows.

2.3.1 Completeness

Each site has the overall objective of collecting 100 percent of the weekly samples and of providing full documentation for each on the MOF. Specific goals are to:

1. Report all precipitation amounts and types.
2. Collect weekly, wet-only deposition samples for chemical analysis that are representative of the total precipitation that fell.
3. Submit one thoroughly documented sample each week to the HAL.
4. Verify the correct operation of all equipment used at the field collection site and the field laboratory.
5. Maintain the precipitation measurement and sampling equipment in good working order to minimize downtime and faulty operation.
6. Verify that HAL printouts of data sent from the site are complete and accurate.
7. Minimize the invalidation of data resulting from procedural errors.

2.3.2 Precision

Precision goals are to:

1. Measure precipitation amounts with the stated precision of the Belfort 5-780 precipitation gauge.
2. Collect a volume of precipitation (rain, snow, or a mixed sample) on a weekly basis that is within 15 percent of the volume recorded by a collocated Belfort 5-780 precipitation gauge.

2.3.3 Bias

It is the objective of the MDN network to compare quantitative measurements made at field

sites to reference materials so that bias may be calculated. Specific bias goals for the field measurements will be defined for the weight of the precipitation sample, the rain gauge depth, and the collector catch efficiency similar to those defined in the NADP QAP Table 2-1.

2.3.4 Comparability

Comparability objectives for MDN field operations are to ensure that all aspects of field procedures including sample collection and documentation are equivalent throughout the network and over the life of the network. Specific goals to accomplish this are to:

1. Use identical equipment for sample collection and precipitation depth measurements.
2. Use standardized collection and sample handling procedures and standardized on-site measurement techniques.
3. Have a site liaison at the HAL apply QC and give advice consistently to each site.
4. Have site personnel receive the same training and utilize the same manuals and instructional materials.

2.3.5 Site and Sample Representativeness

The MDN monitoring program has representativeness objectives for monitoring locations as well as for the samples collected for chemistry. These objectives are (1) to obtain and analyze individual samples which are qualitatively and quantitatively representative of the precipitation that fell (sample representativeness), and (2) to obtain network data that represent broad-scale geographical patterns in concentrations and deposition (spatial representativeness). Specific goals are given below.

Sample Representativeness. The goals are to:

1. Collect a sample for chemical analysis that is representative both in the amount and type (rain, snow, etc.) of the total precipitation that fell.

2. Maintain the integrity of the precipitation sample through all stages of sample handling and chemical analysis.

Spatial Representativeness.

MDN recognizes that the representativeness of a given site location, or of the distribution of a

group of sites, is best determined in the context of the planned application of the data. The MDN will use the NADP general siting criteria in an attempt to obtain samples that are regionally representative, i.e., samples which are indicative of broad geographical patterns of deposition and are not markedly influenced by local emissions. Regional criteria will be relaxed in perhaps as many as half of the MDN sites in order to research Hg deposition in biologically or ecologically important areas. In addition, the program seeks to identify and document any conditions or geographical features which might compromise the regional representativeness of a site, so that data users can take this information into account in interpreting the data. Specific goals are to:

1. Ensure that sites meet the criteria established in Instruction Manual: Site Selection and Installation (Bigelow, 1984). These criteria are summarized in Figure 2-1 in the NADP QAP.

2. Ensure that all conditions that can potentially compromise the regional representativeness of a site are identified and documented, and that this information is available to data users.

The documentation of the site description questionnaire and the establishment of the MDN site files will be managed by the Program Office. These site files will be available to HAL and to the QA Manager to help ensure that the MDN sites meet the NADP Siting Criteria.

2.4 SAMPLE COLLECTION

The MDN protocols currently include a Field Standard Operating Procedure and a MDN Observer Form (MOF). A special collector has been designed for the MDN to preserve the integrity of the collected samples and to provide flexibility to expand into other analytes (Vermette et al., 1994). The MDN collector utilizes two sampling trains under an Aerochem Metrics wet/dry precipitation collector's wet-side lid. One of acid-cleaned and baked glass is for Hg. The modifications to the Aerochem Metric sampler are being done at the Illinois State Water Survey and then shipped to the sites.

Standard procedures for the handling of the mercury samples as well as for checking, and maintaining the MDN collector will be provided in a manual to all site operators (Vermette, 1994). The location of instruments at existing NADP/NTN sites will follow procedures now being used for

NADP/NTN collocated samplers. However, a separate rain gauge will not be required. Instead a sample volume record for the MDN collector will be compared with the NADP/NTN sample volume and a calculated rain gauge precipitation volume. If sample volumes are within the ±range of previously determined collocated rain gauge values, we will assume that the MDN collector operated correctly. The MDN Aerochem Metrics collector will not be slaved to an NADP/NTN sampler. This will allow identification of gross lid-opening failures, but the NADP/NTN precipitation depth record will be used for the calculation of total Hg deposition. At non-NADP/NTN sites, a Belfort rain gauge will be required and follow the same operating procedure as currently exists in NADP/NTN monitoring sites.

Approximately half of the MDN sites will be at existing NADP/NTN sites. As with NADP/NTN, MDN will be a weekly network, where site operators will be instructed to visit their site each Tuesday at 9:00 am. A sample change will be made regardless of sample volume. The exposed sampling train (bottle, funnel and capillary tube) will be removed from the sampler (the collection bottle is capped) and replaced with cleaned ones received each week from the HAL. The exposed sampling train will be brought to the field laboratory where the MOF will be completed. The sampling train and MOF will then be packed for shipment and sent to the analytical laboratory by 2nd day UPS or Federal Express no later than the following day.

2.5 RECORD KEEPING

Information on the sample, the weather during the week, activities near the collector, and collector performance are recorded on the MOF. This is a carbonless, triplicate, standardized form used to record field data. The first two sheets of the MOF and the rain gauge chart are sent to the HAL 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 MOF and copies of the rain gauge charts on file for reference. Entries made on the MOF 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 quarterly preliminary data printouts from the HAL.

2.6 QUALITY CONTROL

Several QC checks are made to ensure that the mercury precipitation collector is 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 equipment checks are summarized in Table 2-2 in the NADP QAP.

Field QC will include a travel blank which is an acidified bottle shipped unopened, a field blank which is a low Hg deionized distilled water (DDW) rinse poured through the sample train immediately after the installation of the sample train, and three system blanks which include 1) a sample bottle with acid and with the sampling train in place which are then left for a week without opening the lid and with the motor box unplugged, 2) another system blank will have a low Hg DDW rinse poured through the sampling train, and 3) will leave a known acidified Hg sample in the bottle for a week to test for absorbance. Visual inspection of the sample will utilize existing MDN MOF categories, and sample volume will be verified by bottle volume comparisons with the Belfort rain gauge. Standard rain gauge data can be substituted for the Belfort recorder where available. The MDN collector compartment temperature will be verified by a max/min thermometer located within the encased bottom of the sampler on a weekly basis.

2.7 PERFORMANCE AND SYSTEMS AUDITS

An intersite comparison study to estimate the precision and bias of Hg measurements will need to be implemented for the MDN. Collocated sites will provide data to estimate precision and bias in the network. A decision will need to be made whether the MDN needs a Blind Audit Program similar to the USGS program for the NADP/NTN. A funded program to address issues related to conformance of network protocols on an annual basis will need to be developed (i.e., NADP Site Visitation Program).

2.8 PREVENTIVE MAINTENANCE/SERVICE

2.8.1 Equipment Checks

The site operation manuals (Vermette, 1994 and Bigelow and Dossett, 1988) direct 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 gauge is replaced whenever excessive corrosion is noted.
4. The foam lid seal on the precipitation collector is replaced when needed.

2.8.2 Network Equipment Depot

An inventory of replacement parts for collector and rain gauge components that are prone to failure or excessive wear is maintained at the Program Office. The purpose of the inventory is to minimize the operational lost time that results from equipment failures. The site liaison at the HAL diagnoses and responds to equipment malfunctions, and coordinates NED replacement part needs with the Program Office. In some cases pre-emptive replacement of worn or failing equipment prevents unexpected equipment failures.

2.9 CORRECTIVE ACTION

Tables 2-1 and 2-2 in the NADP QAP 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 MOF, 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 HAL for assistance in correcting the problem.
2. If the need for corrective action is noted at the HAL or Program Office during a review of information submitted from a site, the first step is to alert the site operator via telephone or email so that the site operator may initiate corrective action. If no

action is taken and the problem continues, the HAL site liaison may call the operator again to discuss the need for corrective action.

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.

2.10 REPORTING AND DOCUMENTATION

Results of the site QA/QC activities will be compiled in several types of reports that are distributed to MDN 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. Quarterly HAL preliminary data printouts are sent to each site operator, site sponsor, and the Program Office. These reports are described in Section 4.11.1.
2. A publication titled Quality Assurance Report: MDN Deposition, Monitoring Field Operations will be prepared periodically by the QA Manager. It will summarize QA aspects of field operations.

SECTION 3
LABORATORY OPERATION

3.1 DESCRIPTION

A trace metal analytical laboratory will provide the total Hg analysis of the precipitation samples collected at the MDN sites. The quality assurance plan which follows is the minimum requirement for the laboratory providing service to the program.

3.2 ORGANIZATION AND RESPONSIBILITIES

The Hg analytical laboratory (HAL) is supervised by a project manager. The functions included in the laboratory are: (a) sample processing and site liaison; (b) sample Hg chemical analysis; and (c) material and data quality assurance. The laboratory will be responsible for maintaining a laboratory QA Plan and evaluating laboratory performance related to MDN samples. An annual laboratory QA report will be prepared on the evaluation results and sent to the Program Office.

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. The Hg detection limits and maximum allowable bias relative to the detection limit from the contracted Hg analytical laboratory will need to be defined. Table 3-1 lists the lower limits of detection and minimum acceptable accuracy for Hg analyses below. The analytical methods and practices described in: Bloom, N.S. and Fitzgerald W. F. (1988) Determination of Volatile Mercury Species at the Picogram Level by Low-Temperature Gas Chromatography with Cold-Vapor Atomic Fluorescence Detection *Anal. Chim. Acta*. 208:151, and Standard Operating Procedures for Total Mercury in Aqueous Media by Nicolas Bloom (1996), documented in the HAL QA Plan, will be followed completely. The actual detection limits and bias will be reported annually in laboratory quality assurance reports.

Table 3-1. Mercury Analytical Laboratory limits of detection.

Constituent	Lower Limit of Detection	10 x Lower Limit of Detection	100 x Lower Limit of Detection (or higher)
Required accuracy	+/- 100%	+/- 20%	+/- 10%
Hg	.02 ng/L	0.2 ng/L	2ng/L

3.4 SAMPLE PROCESSING AND SITE RESUPPLY

3.4.1 Sample Processing

Upon receipt at HAL the samples are logged in with all the information on the MOF entered into an electronic form of the MOF (EMOF) on a computer, together with sample identification number. In addition, a copy of the MOF 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 shipping requirements, and the assignment of an analytical processing code. Any questions concerning the handling of samples or the MOF are immediately directed to the site operator for clarification.

The samples will be unpacked in a clean air station, where various solutions will be added to the sample bottle to preserve the Hg compounds and to remove any absorbed Hg from the bottle walls and allow leaching of suspended matter. Analysis of the samples will be initiated as soon as possible upon receipt of samples at the analytical laboratory. The samples will be maintained in their original collection bottle and removed into a sample vial upon analysis. The precipitation sample will be treated with strong oxidants to destroy any organic matter and release any mercury to the Hg(II) oxidation state. The mercury in the sample will then be reduced and converted to the volatile elemental state. A clean nitrogen purge will then be used to sweep elemental mercury from the samples onto a gold sand trap that concentrates the mercury. The trap is thermally desorbed and the mercury swept into the flow of a cold vapor atomic fluorescent detection system. A HAL Standard Operating Procedure (SOP) describes the operational procedures for the receipt and check-in of MDN samples by the HAL. This document also describes the details of the incoming sample

handling and coding procedures.

Sampling protocol (SP) and screening level (SL) codes are assigned at the HAL, and passed to the Program Office. The SP/SL codes are used to assist the laboratory analyst in documenting cautions to be used in evaluating the entire QC document trail, and finally the sample validity. In addition, the quality assurance samples are pulled from the analytical lab data set into quarterly and annual HAL QA reports. The laboratory report for each week's run will also contain, standards, SRMs, spike recoveries, and duplicate analyses utilized in the lab for quality control, and at the Program Office for quality assurance. Quarterly the analytical laboratory will send every site a report containing information recorded on the MOF and analytical results. The report will include computer-generated messages concerning errors or potential problems at the site.

3.4.2 Site Resupply

The MDN 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. Shipping boxes for transporting cleaned sampling train (glass bottle, capillary tubing, and funnel in polyethylene bags).

2. MDN Observer Forms (MOF).

8. Rain gauge charts and ink for Belfort 5-780 Universal rain gauges.

9. Replacement Teflon-wrapped foam pad and polycarbonate lid seals for the modified Aerochem Metrics collector.

3.5 SAMPLE ANALYSIS METHODS

By employing ultraclean laboratory techniques the MDN will assess accurately atmospheric concentrations and deposition rates of Hg in near-background conditions. Analytical techniques suitable for Hg determination at the picogram and nanogram levels in air are based on cold vapor atomic fluorescence spectrometry (Bloom and Fitzgerald, 1988). This detector is inexpensive with an extremely good detection limit, 0.3 pg. The system can also be coupled to a low-temperature gas chromatographic system and applied in Hg speciation studies.

An accurate collection and handling of aqueous samples for low-level determination of Hg must include aspects on the representativeness of the sample, contamination sources, as well as preservation and storage of the sample before analysis. Bloom (1995) describes the ultraclean sample handling and storage protocols our network will follow.

After collection, samples are returned to the analytical laboratory by overnight courier. Upon arrival, the bottles are unpacked in the clean air station, and 1 mL of 0.2 N BrCl in HCl is added to each bottle. The BrCl solution, which serves to oxidize all Hg compounds to Hg (II) is pre-analyzed, and found to be low in Hg (i.e., <0.05 ng/mL) prior to use as a lab reagent. Following addition, the caps are replaced, and the bottles shaken several times over a period of at least 4 hours to remove any absorbed Hg from the bottle walls and to allow leaching of suspended matter. The strong oxidant destroys any organic matter and release any mercury to the Hg (II) oxidation state. The mercury in the sample is then reduced and converted to the volatile elemental state. A clean nitrogen purge is used to sweep elemental mercury from the samples onto a gold sand trap that concentrates the mercury. The trap is thermally desorbed and the mercury swept into the flow of a cold vapor atomic fluorescent detection system. Quality is assured through calibration and testing of the oxidation, purging, and detection system, and the routine analysis of matrix spike recoveries.

Total mercury as defined by this analytical method means all BrCl oxidizable mercury compounds found in aqueous solution. This includes, but is not limited to Hg(II), Hg(0), strongly organo-complexed Hg(II) compounds, adsorbed particulate Hg, and several tested covalently bound organo-mercurials (i.e. CH_3HgCl, $(CH_3)_2Hg$, $C_6H_5HgOOCCH_3$). Due to the BrCl oxidation step, there are no observed interferences with the total Hg methodology when properly carried out.

3.6 CALIBRATION PROCEDURES

The analytical system will be calibrated with aqueous standards spanning a linear range beyond the highest expected measurements. The initial calibration curve will contain four or more non-zero points, and two bubbler blanks. For more detail on the calibration procedures for the Hg analytical laboratory see Bloom's document titled Total Mercury in Aqueous Media (1996).

3.7 RECORD KEEPING

Laboratory personnel will have access to records for review and assessment of problems. Paper records will be maintained for no less than one year following formal publication in the NADP/NTN data reports. All laboratory log books will be archived at the HAL for the duration of the contract. Once the data have been fully screened and non-conforming data appropriately flagged, the data is sent to the NADP Program Office for input to their database and data dissemination.

3.8 QUALITY CONTROL

A quality assurance program for Hg in wet deposition requires stringent laboratory conditions and careful control over all aspects of the analyses. Each step in the analytical process 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 analytical laboratory will need to develop quality control procedures to provide the necessary checks at all processing stages.

3.8.1 General Laboratory Procedures

Precipitation samples are collected and stored in 1 liter borosilicate glass bottles with Teflon-lined phenolic resin caps. The bottles are initially cleaned at the analytical laboratory by heating to 70^{o}C for 48 hours in 4 N HCl, followed by thorough rinsing in low-Hg (<1 ng/L) deionized distilled water (DDW). The caps are cleaned by soaking for 48 hours in 0.1 N HCl at room temperature. After this, and before each subsequent use, the bottles are filled with low Hg-DDW, to which 5 mL of BrCl in concentrated HCl has been added, the caps replaced, and the bottles placed in a low Hg (<15ng/m^3) class 100 clean air station for 24 hours to soak. Bottles are then emptied, thoroughly rinsed with low-Hg DDW, and allowed to dry for several hours in a low-Hg clean air station. To each bottle is added 20 ±5 mL of 0.12 N HCl(<0.5 pg Hg/mL), and the lids tightly fastened. While still in the clean air station, the bottles are enclosed in new polyethylene bags, and then packed into specifically constructed shipping containers. Prior to the first use, the acid in several sample bottles treated in this way is checked after one week of storage to verify no perceptible contamination (<0.01 ng Hg/bottle) due to the containers. These method have been in use for several years (Fitzgerald and Gill, 1979; Bloom and Crecelius, 1983).

The funnel and capillary tube are initially cleaned by a thorough rinsing in HNO_3, followed

by a thorough low Hg-DDW rinse. The openings of the funnel and capillary tube are wrapped in aluminum foil (dull side facing in and open sufficiently to allow contaminants to escape the glassware) and immediately placed in a muffle furnace to be baked at 950°F for a minimum of 4 hours. Upon removal, the funnel and capillary tube are placed in separate new polyethylene bags. Similar procedures are followed subsequent to each use in the field.

HAL uses 18 megohm ultra-pure deionized water starting from a prepurified source. Water will be monitored for mercury especially after ion exchange beds are changed. The laboratory air will be monitored to assure it is low in both particulate and gaseous mercury.

3.8.2 Instrumental Procedures

The determination of total Hg in precipitation is controlled by analytical batch. An analytical batch is a subset of samples oxidized with the same batch of reagents, which are analyzed together on the same date. A batch may be from one to as many 20 samples. Each batch must be accompanied by at least 3 bubbler blanks, an ongoing precision and recovery sample (i.e., a standard reference material, SRM), one duplicate analyses, and one matrix spike and one matrix spike duplicate. Bubbler blanks are analyzed to demonstrate freedom from system contamination. The mean bubbler blank for a day, if within acceptance criteria, is subtracted from all peaks prior to the calculation of results. If more than 20 samples are run in a day, then an additional bubbler blank, ongoing precision and recovery samples, duplicate, and matrix spike must be analyzed for each additional ten or fewer samples. Reagent blanks for this determination are required at the time that the batch of reagents (bromine monochloride plus hydroxylamine hydrochloride) are made, with verification (in triplicate) on a monthly basis until a new batch of reagents are needed.

There are currently no SRMs available for low level Hg in water. Therefore, laboratory precision and accuracy must be verified by low-level spike recoveries and by intercomparison with other established laboratories using a technique with similar performance characteristics. The methodology for formulating the low level spike recovery sample is described by Bloom in Total Mercury in Aqueous Media (1996). Because of the lack of SRMs for low level Hg in precipitation, the matrix spike and matrix spike duplicates at a rate of one per 10 samples will serve as the check of ongoing precision and accuracy.

3.8.3 Replicate Samples

At least one in every 10 samples is analyzed in duplicate and one in every ten is analyzed with a matrix spike recovery. For each day of analysis, at least three system blanks are analyzed, the results of which are added to the reagent blanks which are determined once for each batch of reagents.

3.8.4 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. 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.

Once the analysis of the sample is completed, the data are entered into the database and are checked visually against the field form record numbers and the analytical report record numbers, as well as for verification of the entered value. The database is backed-up quarterly with the addition of new sample values.

3.9 PERFORMANCE AND SYSTEMS AUDITS

Internally, current information on the characteristics (i.e., precision, bias, detection limit) of analytical methods is provided by a continuous quality assurance monitoring program operated by the laboratory QA officer.

The laboratory will participate in a formal external quality assurance program, yet to be defined, but may include the following: a blind sample audit, an interlaboratory comparison, and periodic on-site reviews by NADP/NTN subcommittee members and MDN advocates.

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 QA officer 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. The laboratory's QA officer 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 QA manager who initiates, tracks, and documents the remedial actions.

3.12 REPORTING AND DOCUMENTATION

Reports will be written to include the results and evaluation of internal quality assurance program analyses and documentation of problems and associated corrective actions. The reports will also include documentation of method changes. These reports will be summarized annually by the HAL project manager and submitted to the Program Office.

Documents required to support the QA/QC activities of the analytical laboratory consist of various log books, 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 QA officer. 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.

5. 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 Program Office.

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 MDN monitoring sites, and the HAL will be transferred to the Program 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 HAL, and the Program Office. Final responsibility for data management activities resides with the NADP Coordinator. All data management procedures are subject to approval by the NADP Technical Committee.

The various data management groups exchange information that ultimately results in the creation of the network database. 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.

4.2.1 MDN Monitoring Sites

MDN field sites submit a site description questionnaire (Bigelow, 1984) documenting the sites' location, administration, instrumentation, and emission source profile to the Program Office. In addition, each site submits a weekly MOF that contains information about the sample submitted to the HAL. This information includes a definition of the sampling period, a report on the sample

condition, weather information, and the results of QC checks performed. The MOF is accompanied by a recording rain gauge chart. The site operator is responsible for submitting data to the HAL. The operator is also responsible for remedying incomplete or inaccurate site data.

4.2.2 The Mercury Analytical Laboratory (HAL)

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

The HAL project manager has overall responsibility for the laboratory's MDN data management activities. The HAL site liaison has responsibility for information exchange between the HAL 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 a laboratory QA officer. The HAL project manager is responsible for all additions, deletions, and updates to the MDN data.

4.2.3 NADP/NTN Program Office

The Program 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 coordinator at the Program Office has overall responsibility for network data

management activities. The NADP/NTN database manager with the MDN coordinator are responsible for receiving, verifying, transforming, and updating network data submitted by the site operators, and the HAL, and they have overall responsibility for documenting data completeness, and summarizing and reporting data. The HAL site liaison is responsible for information exchange between the sites and the Program Office. This includes documenting site operational problems, changes in site configuration and location, and maintaining records of remedial actions at sites.

The MDN coordinator is responsible for final validation and characterizations of network data, accumulation of network documentation, and assessment of data quality. Because the MDN coordinator 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 database manager and MDN coordinator in entering, transferring, and transforming data. They also assist in implementing software packages and writing computer programs that manipulate network data. The MDN coordinator, and other MDN data management staff report to the NADP coordinator.

4.3 OBJECTIVES AND GOALS

The achievement of the overall objectives of the MDN 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 will need to be defined and will be the similar to NADP completeness goals.

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 based on NADP goals and 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.
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 NADP 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 MDN monitoring program is to provide users of MDN 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 HAL 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 quarterly.
3. The HAL transfers all required final data and supporting documentation to the Program Office within four months of sample submission.
4. Quality and 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 site description questionnaire which is slightly modified for the MDN. This questionnaire provides the initial documentation for site location, administration, equipment, and emission source records. The site operator submits this information to the Program Office for review. Original site documentation is maintained at the Program Office in storage files, one per site and made available to the HAL.

4.4.2 Weekly Field Information

The Standard Operating Procedures for the MDN (Welker, 1996) contain the site operator's instructions for completing the weekly MOF and for interpreting the weekly rain gauge chart. When completed this information is forwarded to the HAL by the site operator each week.

At the HAL, each MOF and rain gauge chart is coded with a unique, alpha-numeric laboratory identification. The information from the completed MOF is entered into an electronic MOF (EMOF). Additional information describing sample leakage, gross contamination, compliance with sample shipping requirements, and confirmation of sample weight are also entered into the EMOF. The EMOF is eventually electronically transmitted to the Program Office, and then entered into processing and validation programs. These programs check the EMOF data and identify any discrepancies. Discrepancies are resolved manually by the database manager and HAL project officer.

4.4.3 Chemical Analysis Results

The analytical results are entered into the EMOF at the HAL. Any errors detected during this keystroke-by-keystroke verification step are corrected. These verified files are then merged with preliminary field data from the MOF to form the preliminary MDN files that are transferred quarterly to the Program Office.

In both automated and manual data acquisition, laboratory analysts are responsible for the correct entry and transformation of instrumentation output.

4.4.4 Merged Field and Chemical Analysis Data

HAL preliminary data that are validated by the laboratory QA officer before being transferred electronically to the Program Office. At the Program Office, time fields are transformed from EST to Greenwich Mean Time (GMT) and precipitation data are transformed from inches of precipitation to millimeters of precipitation.

At the Program Office, computer programs reformat the data for QC testing and then enter it into a database management system (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 HAL, from site audits, and from the review of information supplied to the Program 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 database. 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. Computer programs and descriptions of file formats reside in a single directory in the computer system at the Program Office.

4.5 DATA VERIFICATION AND VALIDATION

4.5.1 Site Description Records

Once the site description questionnaire information is received at the Program Office it is reviewed 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 Program 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.

4.5.2 Weekly Field Information

Immediately after the data from the MOF have been entered into the EMOF, the HAL 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 MOF and rain gauge data are verified and corrections are made. A validation code, known as a sample protocol (SP) code, is also assigned to each deposition sample to indicate departures from standard sample collection procedures that may have compromised sample integrity. The HAL site liaison additionally maintains, for reference purposes, a record of all oral and written communications with site personnel.

4.5.3 Chemical Analysis Results

The verification and validation of chemical analysis results is described in the Laboratory

Section of this Quality Assurance Plan (Section 3.0).

4.5.4 Merged Field and Chemical Analysis Data

The HAL site liaison receives the MOFs, rain gauge charts, and all other accumulated information relevant to the validation of site records. Screening level (SL) codes are assigned to samples that were contaminated or that were identified as having been handled in a manner inconsistent with field or laboratory protocols. SL codes are also assigned on the basis of the HAL project officers review of MOFs, rain gauge charts, and the HAL-site operator correspondence. After this review, the MOF information and the analytical data are entered into the EMOF and sent to the Program Office.

Final validation of MDN data takes place at the Program Office under the direction of the NADP/NTN database manager. The data transferred to the Program Office are validated using data validation rules maintained in a special computer file at the Program Office. These rules use the SP and SL codes, but group the samples into less specific categories.

4.6 RECORD KEEPING

4.6.1 Network Data

Forms that originate at field sites (MOFs and rain gauge charts) are archived at the HAL. Other site records that originate at the HAL, such as transcripts of communications and other correspondence, are attached to the second of the three-part MOF and archived at the HAL. Results of analytical measurements including original paper records and quality assurance results from instrumentation that are filed by the analysts and the laboratory QA officer are also archived at the HAL.

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

Records stored at both the HAL and Program Office are stored for the life of the project. At the HAL both paper and electronic records are kept under the supervision of the HAL project manager. At the Program Office MDN records are maintained under the supervision of the

coordinator.

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 QA 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 database manager monitors the frequency of record updates in network data.

4.7 QUALITY CONTROL

4.7.1 Data Collection, Entry, Transfer, and Transformation

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 FTP (file transfer protocol).

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

Quarterly, the HAL sends each site a computer generated printout of the information supplied on the MOF, analytical results, along with computer generated comments concerning errors or potential problems at the site. Site operators are asked to respond to any deficiencies noted on the printouts and to verify the MOF information contained therein (also see Section 4.11.1).

At the HAL, assigned data validation codes (protocol and level codes) are reviewed quarterly

by reviewing the coding of 10-20 randomly selected samples with the people responsible for assigning codes.

At the Program Office a 25 percent random subset of each batch of weekly MOFs received from the HAL is rekeyed and loaded into a separate computer file. Information common to the MOF 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 HAL 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 every two years. Results of the audit are reported to the Technical Committee.

4.9 PREVENTIVE MAINTENANCE/SERVICE

At the HAL, a system of regular deliberate duplication of computer files on magnetic tapes and diskettes is used to maintain and prevent loss of records. 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 Program Office, preventive maintenance consists of daily tape back-ups of all computer disks by the systems manager at the Program Office 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 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 will follow 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 if the change has an impact on previously finalized data.

4.11 DATA REPORTING AND DOCUMENTATION

4.11.1 HAL Preliminary Data Reports

The HAL sends the site operator and site sponsor a quarterly report that contains preliminary results of the HAL's chemical analysis and information contained on the MOF. Site operators and site sponsors are expected to review and verify the information in the reports and to respond to the computer-generated comments, as necessary. Any other information regarding data quality resulting from this review is forwarded to the HAL. Responses are made by annotating the appropriate report page and mailing it back to the HAL in the shipping container during the next regularly scheduled sample submission.

4.11.2 Reports of Weekly Data

Site operators and site sponsors 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.

4.11.3 Annual Data Reports

The annual data report summarizes the chemistry of precipitation samples collected at sites in the MDN 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.

The format for how the mercury data will be incorporated into the annual data reports needs to be determined.

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

4.11.4 User-Requested Data Reports

Custom requests are honored whenever possible.

4.11.5 Changes in Previously Reported Network Data

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 HAL project manager reviews any changes in the chemical analysis of samples or data management activities at the HAL. This review 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 Program Office.

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 Program Office.

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