

**Quality Assurance Plan  
Mercury Analytical Laboratory,  
2006**



National Atmospheric  
Deposition Program

## Quality Assurance Plan Approval Form

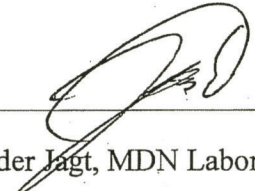
The Quality Assurance Plan has been reviewed and approved by the following authorized National Atmospheric Deposition Program, Frontier Geosciences, signatories for quality assurance documents.

Signature  \_\_\_\_\_

Date 7/14/08

David Gay, Program Coordinator,

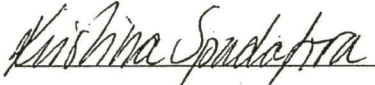
National Atmospheric Deposition Program

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Date 07/14/2008

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## Table of Contents

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<b>List of Figures</b> .....	ii
<b>Section A: Program Overview</b> .....	3
1. Introduction .....	4
2. Organization and Responsibilities .....	5
3. Quality Assurance .....	6
4. Facilities and Equipment .....	8
5. MDN Operations .....	9
<b>Section B: Field Operations</b> .....	15
1. Description .....	17
<b>Section C: Laboratory Operations</b> .....	23
1. Laboratory Procedures.....	25
2. Sample analysis .....	26
3. Performance and System Audits .....	29
4. Corrective Action .....	29
<b>Section D: Data Management Operations</b> .....	31
1. Preventive Maintenance/Service .....	33
2. Data Management Operations .....	33
3. Objectives And Goals.....	34
4. Data collection, entry and transfer.....	36
5. Data Verification And Validation .....	36
6. Record Keeping .....	37
<b>Frontier GeoSciences – MDN Specific SOPs</b> .....	38
<b>Frontier GeoSciences – Supplemental SOPs</b> .....	39

# List of Figures

<b>Figure 1:</b> Mercury Analytical Laboratory organizational chart .....	5
<b>Figure 2:</b> Sample analysis flow chart.....	11
<b>Figure 3:</b> Lab Data Management Flowchart .....	12
<b>Figure 4:</b> MDN Equipment Flowchart .....	19
<b>Figure 5:</b> MDN Specific SOP List .....	38
<b>Figure 6:</b> Supplemental SOP List .....	39

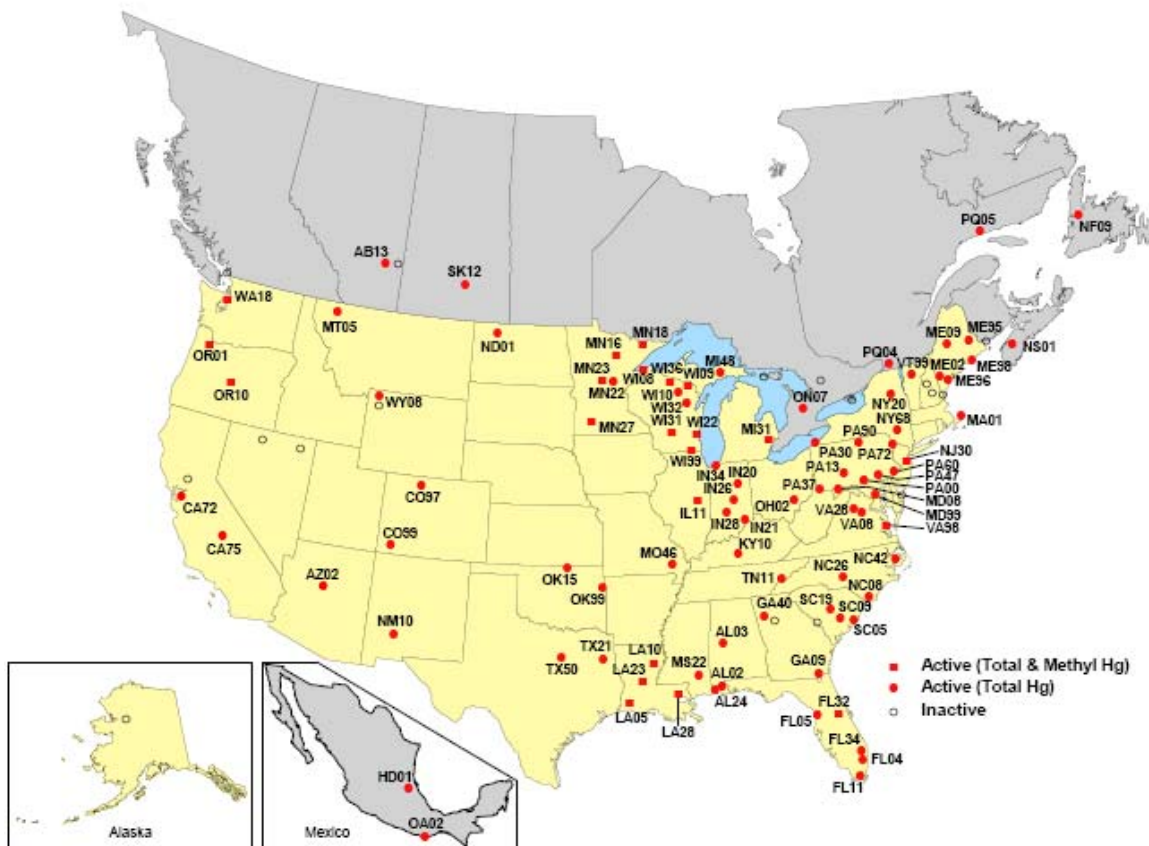
## Definitions of Acronyms and Abbreviations

<b>CAL</b>	Central Analytical Laboratory
<b>CCB</b>	Continued Calibration Blank
<b>CCV</b>	Continued Calibration Verification
<b>COC</b>	Chain of Custody
<b>CRM</b>	Certified Reference Material
<b>CVAFS</b>	Cold Vapor Atomic Fluorescence Spectrometry
<b>DQO</b>	Data Quality Objectives
<b>EMOF</b>	Electronic Mercury Observer Form
<b>HAL</b>	Mercury (Hg) Analytical Lab
<b>ICB</b>	Initial Calibration Blank
<b>ICV</b>	Initial Calibration Verification
<b>MD</b>	Matrix Duplicate
<b>MDL</b>	Method Detection Limit
<b>MDN</b>	Mercury Deposition Network
<b>MOF</b>	Mercury Observer Form
<b>MS</b>	Matrix Spike
<b>MSD</b>	Matrix Spike Duplicate
<b>NADP</b>	National Atmospheric Deposition Program
<b>NTN</b>	National Trends Network
<b>NED</b>	Network Equipment Depot
<b>PB</b>	Preparation Blanks
<b>PE</b>	Performance Evaluation
<b>PT</b>	Proficiency Test
<b>QA/QC</b>	Quality Assurance/Quality Control
<b>QAP</b>	Quality Assurance Plan
<b>QR</b>	Quality Rating Code
<b>RL</b>	Reporting Limit
<b>RPD</b>	Relative Percent Difference
<b>SOP</b>	Standard Operating Procedure
<b>SRM</b>	Standard Reference Material

# **Section A: Program Overview**

## 1. Introduction

Since January 1996, Frontier GeoSciences Inc. (FGS) has served as the Mercury Analytical Laboratory (HAL) and Site Liaison Center for the Mercury Deposition Network (MDN). The MDN, coordinated through the National Atmospheric Deposition Program (NADP), was designed with the primary objective of quantifying the wet deposition of mercury in North America to determine long-term geographic and temporal distributions. The Network has grown to incorporate over 95 sites in North America.



As HAL, FGS provides site support, sample processing, sample analysis, and data validation services for precipitation samples collected at the NADP/MDN monitoring sites. All these processes must follow documented quality assurance and quality control procedures. The Quality Assurance Plan (QAP) describes these procedures and indicates how they are to be monitored and quantified. The QAP is reviewed annually and updated as necessary.

## 2. Organization and Responsibilities

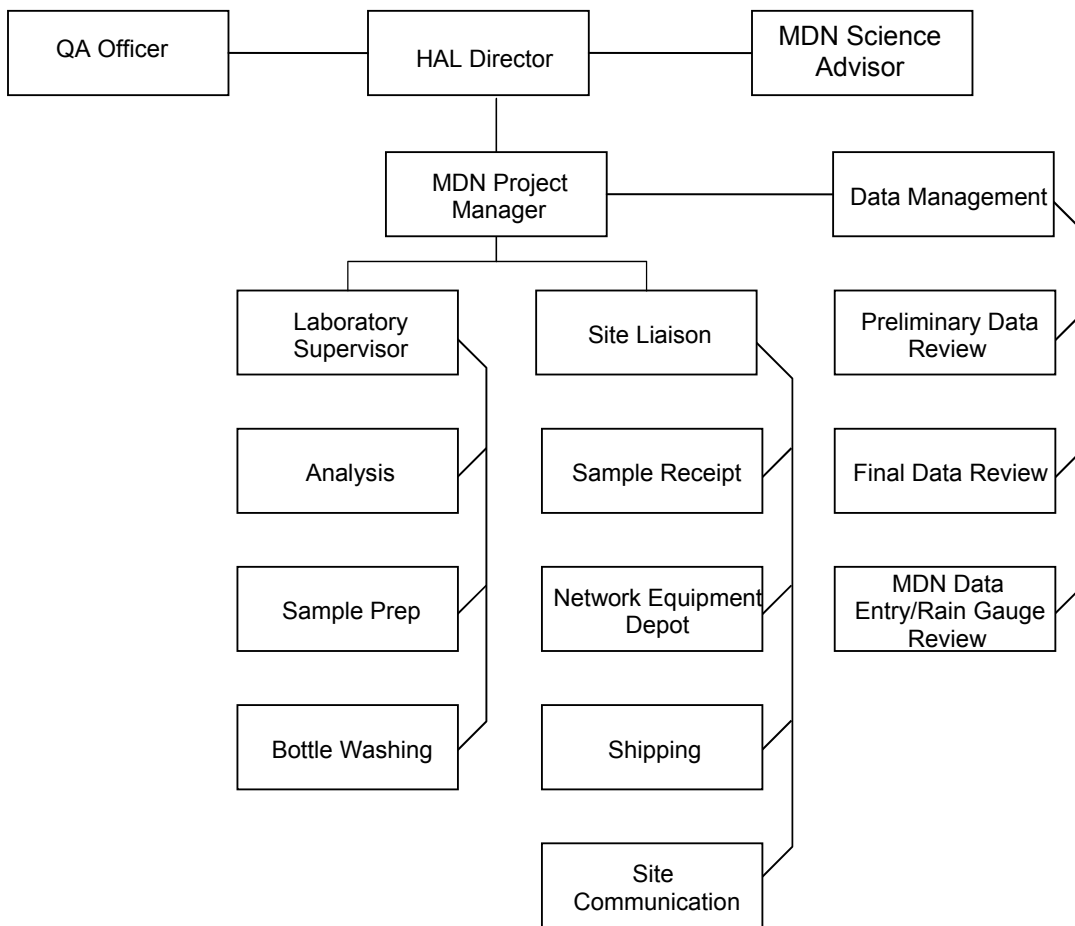


Figure 1: Mercury Analytical Laboratory organizational chart

### 2.1. HAL Director

The HAL Director oversees FGS's involvement in the MDN. The Director serves as the HAL contact for the multiple agencies currently sponsoring the MDN. The Director provides guidance and direction to all HAL staff and maintains proficiency in all aspects of HAL activities including: site selection and equipment installation, equipment troubleshooting, field and laboratory training, analysis and report writing, as well as research on new initiatives.

### 2.2. MDN Project Manager

The MDN Project Manager reports directly to the HAL Director. The Project Manager's goal is to consistently produce data that meets the Data Quality Objectives (DQO) while maintaining required supplies and data turn-around-times, cost effectiveness, sustainable laboratory practices, employee job satisfaction, and supportive customer relations.

The Project Manager has ultimate responsibility for the quality of all analytical laboratory data, reports, practices, and safety. The Project Manager ensures that data meet all quality control requirements, or takes appropriate and documented corrective action if it does not. Finally, it is the Project Manager's responsibility to ensure that all staff members understand and adhere to the QAP and relevant standard operating procedures (SOP).

## 2.3. Quality Assurance Officer

The Quality Assurance (QA) Officer's goal is to continuously improve the laboratory's quality assurance/quality control (QA/QC) processes in a manner consistent with the MDN mission statement. This requires support from the Management Committee and laboratory staff. The QA Officer ensures that all laboratory decisions are considered from a QA standpoint. Specifically, the QA Officer has the following responsibilities relating to laboratory QA systems:

- coordinates training procedures for laboratory staff, including QA orientations and ethics training
- oversees facilities testing programs (reagent water, vats, bottles, equipment, and air)
- investigates rejected datasets and corrective actions
- manages proficiency tests and laboratory intercomparison studies
- maintains controlled documents including the laboratory QAP and SOPs
- provides staff members with QA information as needed
- follows procedures described in the QAP and all applicable SOP
- may deviate from written procedures per FGS-087 Deviation from Policy
- performs other relevant tasks associated with FGS's QA requirements

The QA Officer is responsible for reporting the progress and overall performance of QA/QC measures to the HAL Director. This is communicated by internal audit reports, memorandums, and QA program quarterly reports. The QA Officer works closely with the Project Manager to ensure that all staff members adhere to the QAP and relevant SOP, and that scientific excellence remains FGS's top priority. In the absence of the QA Officer, the Deputy QA Officer carries out the responsibilities of the position.

## 2.4. Technical Staff

The HAL Technical Staff includes analysts, laboratory technicians, and project specific permanent support staff. To ensure high quality, the Technical Staff reads and follows the MDN QAP, adheres to relevant SOPs, and contributes in improving to the overall quality of the HAL and thus the MDN network.

# 3. Quality Assurance

## 3.1. Quality Assurance Policy Statement

FGS is committed to QA, viewing it as both a program and a philosophy. Quality control begins at the bench level, and management continuously works to improve processes with a focus on prevention of analytical problems. FGS's laboratory staff is trained to troubleshoot and initiate corrective actions. Process improvements and problem solving are solicited from the technicians and analysts, and management implements the solutions. This helps keep management informed while at the same time promoting the professional growth of FGS's staff.

FGS is dedicated to providing high-quality data that meets the needs of the MDN. Accurate and precise data depends on these basic principles:

- Sample integrity must be preserved. All documented sample handling procedures for preservation, custody, storage, labeling, and record keeping are followed.
- Trace metal-free ("ultra-clean") sample handling must be employed. Samples that are analyzed for low-level or ambient metals concentrations are handled according to established protocols. This includes the use of Class-100 clean areas, clean room gloves, and pre-tested and approved reagents, water, and equipment. High-level (contaminated) samples are kept segregated from ultra-clean samples during storage and sample preparation.
- Approved analytical methods must be followed. The analyst's fundamental understanding of analytical methods is paramount for effective quality control. Emphasis on scientific



understanding and adherence to procedure is part of every analyst's training. QC results from each method are evaluated to identify and correct method weaknesses, and to detect any need for further training.

- Analytical instrumentation must be in proper working order. Optimum instrument performance is ensured by analyzing daily calibration and performance evaluation samples. Preventative maintenance is performed on a regular basis and is documented in the instrument logbooks.
- Raw data must be properly reduced and accurately transcribed into the correct reporting format.
- Various levels of data review, from acquisition to the final report, are performed to minimize error.

### **3.2. Quality Assurance Objectives**

HAL data quality is assessed against FGS's DQO to ensure production of high-quality coherent data. The DQO consist of five elements: precision, accuracy (bias), representativeness, comparability, and completeness. These elements are evaluated annually and the results are presented in Annual QA Reports.

- Precision is a measure of our ability to use our methods to analyze a sample repeatedly and get the same results each time. To demonstrate precision of a method, sample duplicates are analyzed and the results compared. The acceptance criteria for Matrix Duplicates is  $\leq 25\%$  RPD
- Accuracy or bias is a measure of how close the result is to the true or expected value of the target analyte in the sample. Accuracy may be determined by the analysis of reference materials, blank spikes, or matrix spikes where the results can be compared with a true or expected value. The acceptance criteria for Reference Materials and Matrix Spikes is 75-125% RPD.
- Representativeness describes how well a single sample can characterize the conditions of the entire sample population. Appropriate sampling techniques and artifact-free procedures, combined with sample homogenization, help achieve representative data.
- Comparability is a particularly important QA criterion for long-term projects. Individual data sets are evaluated with respect to other data from the same project to ensure the validity of trends in the data.
- Completeness is a measure of how many collected data points are usable. HAL strives for at least 95% analytical data completeness for the MDN project.

### **3.3. Proficiency Testing Program**

As part of good laboratory practice, FGS participates in proficiency test studies at least four times per year. We currently participate in semi-annual New York Department of Health performance studies for Non-potable Water/Solid & Chemical Materials/Air & Emissions Chemistry Proficiency Test. We also participate in two water pollution proficiency tests each year. These are supplied by a licensed and approved commercial provider. Results for each of these studies are submitted to all of FGS's accreditors and are available to any client upon request.

### **3.4. Laboratory Intercomparison Studies**

Each year, FGS takes part in several laboratory intercomparison studies, spanning a wide range of matrices including biota, sediment, estuarine water, and fresh water. FGS is a regular participant in studies prepared by the United States Geological Survey (USGS), the National Research Council — Canada, the International Atomic Energy Agency, and the National Water Research Institute — Canada. Typically, our larger projects specifically include additional intercomparison studies. HAL participates with a USGS sponsored MDN specific interlaboratory comparison program.

### 3.5. Training Program

Staff members are trained in new skills or methods by a mentorship process. Staff members are assigned to their immediate supervisor or a senior co-worker and trained according to the following steps:

- reading the SOPs
- observing performance of the method
- closer reading of the SOPs, associated literature, and other notes
- supervised practice of the method on non-critical work until the supervisor is satisfied that the employee is competent
- unsupervised practice of the method, with review by the trainer and supervisor
- unsupervised performance of the method

Completion of these steps is documented on a training form, which is signed by the trainee and the Project Manager. Employee training files are reviewed quarterly during internal audits, and are reported as part of the FGS QA Program Quarterly Report.

## 4. Facilities and Equipment

FGS's 18,000 ft<sup>2</sup> research and analytical laboratory facilities are located in downtown Seattle, Washington. The location is close to Seattle-Tacoma International Airport, the University of Washington, and National Oceanic and Atmospheric Administration (NOAA). HAL has a dedicated MDN mercury analysis laboratory as well as a dedicated MDN shipping and receiving area, MDN bottle washing room, MDN staging area, and staff offices. FGS's entire facility is secure.

The laboratories are served by a custom-designed HVAC system, providing an atmosphere that is clean and well isolated from outside dust and dirt. Each laboratory atmosphere is monitored for gaseous mercury and appropriate action is taken if it exceeds 25ng/m<sup>3</sup> in any location. Water systems are also checked weekly for trace metals content. FGS uses continuously monitored acid neutralization discharge systems for liquid acid-waste disposal. Disposal of all other toxic materials is carried out under contract with a certified disposal company. The entire FGS space is periodically inspected for compliance with all city and state code requirements for fire, emissions, and storage of low-level radioactive samples.

The offices are equipped with document production equipment including laser printers, document and image-processing software, high-volume photographic-quality color printer, large-capacity collating copiers, and a binding machine. A LAN connects staff computers and printers for local access, as well as providing external e-mail, fax, and Internet access. FGS also maintains a web site at [www.frontiergeosciences.com](http://www.frontiergeosciences.com), and has a FedEx Powership shipping computer with access to FedEx pick-up as late as 17:00 Pacific time. Staff is present on Saturdays to receive sample shipments.

### 4.1. HAL Capital Equipment for Analytical Use

Quantity	Instrumentation
6	Cold Vapor Atomic Fluorescence Hg Detector
3	Isothermal GC for Hg Speciation
2	Class-100 Clean Air Hood
1	Milli-Q Reagent Water System
6	Methyl Hg Distillation Units
1	Gold Sputter Coater
1	RO Reagent Water System

## 4.2. Ultra Clean Facilities Monitoring

### 4.2.1. Bottle and Acid Vat Monitoring

Ensuring that our sample collection containers are appropriately cleaned for ambient water sampling is vitally important to FGS. A random, monthly bottle monitoring program gives quantitative evidence that procedures and their practice are contaminant-free. Every month, twenty bottles of each type (Teflon and polyethylene) are tested for a suite of trace metals. Bottles are randomly chosen “off-the-shelf,” just as bottles would be for shipments to clients. 95% of the bottles tested must show total mercury levels of less than 1ng/L; otherwise, another batch of 20 bottles is tested and the QA officer is notified so that appropriate corrective action may be taken.

Acid vats in the bottle washing room are also tested monthly. Control limits for each test are detailed in FGS-007 Cleaning of Sampling Equipment and Bottles, FGS-065 Cleaning of Sampling Equipment and Bottles for Analysis of Trace Metals, and FGS-096 Acid Vat Monitoring Program. Records of each test are maintained by the QA Office and are available upon request.

### 4.2.2. Air Monitoring

FGS’s mercury analyses require ultra-low levels of mercury in laboratory air. All laboratories at FGS are monitored for mercury contamination by the method described in FGS-067 Passive Diffusion Monitoring for Gas Phase Atmospheric Mercury. Each month, samples are retrieved and analyzed. The action limit for laboratory air is 25ng/m<sup>3</sup>. If a laboratory exceeds the action limit, corrective action is taken and documented. Records of each test are maintained by the QA Office and are available upon request.

### 4.2.3. Reagent Water Monitoring

All reagent water is monitored for a variety of analytes on a weekly basis. Acceptable results from these tests confirm each water system’s suitability for analytical use. If a system produces unacceptable results, it is sequestered until subsequent analyses verify freedom from contamination. Control limits and records of each test are maintained by the QA Office and are available upon request.

## 5. MDN Operations

### 5.1. Sample Processing

The HAL sample processing and analysis scheme is illustrated in Figure 2. Upon receipt at HAL, samples are received in a designated shipping and receiving room. Immediately after pulling the sample from the cooler, the MDN bottle ID is verified against the Mercury Observer Form (MOF). Any site issues are documented in the MDN Site Issues Logbook and the Site Liaison notified so relevant sample information can be gathered. Still encased in the bottle bags, the samples are transported to the Mercury Atmospheric Deposition and Emissions (MADE) receiving bench where the sample is checked for leaks and any observations regarding the sample state are noted. The MOF is completed at the bench and the information immediately entered in the MDN Data Management System. The sample and MOF are designated a run number that describes the year and batch the sample will be contained in. There are thirty samples per batch.

Once a batch of thirty samples is collected, all samples in the batch are preserved to 1% BrCl in the original sample bottle. This step destroys any organic matter and releases any mercury to the Hg(II) oxidation state. Once preserved, the sample must stand overnight to ensure total oxidation. The sample is reduced during the analytical process and converted to the volatile elemental state. The elemental mercury is passed onto a gold trap where it is thermally desorbed into the flow of a cold vapor atomic fluorescent detection system (CVAFS). The receipt procedures are outlined in

detail in FGS MDN-02 Sample Receipt Procedures and the analysis is detailed in FGS MDN-05 THg Sample Analysis.

Some samples are also analyzed for methylmercury and are treated differently than others. The methylmercury samples need to be acidified and refrigerated before a portion is taken for methylmercury analysis. After a portion is taken for methylmercury, the sample is put back into a total mercury analytical batch. For a detailed description of the methylmercury procedures please refer to FGS MDN-06 Methyl Mercury Preservation, Splits and Comps, FGS MDN-07 Distillation of MDN Precipitation Samples for Methyl Mercury Analysis and FGS MDN-08 Methyl Mercury Calibration and Analysis.

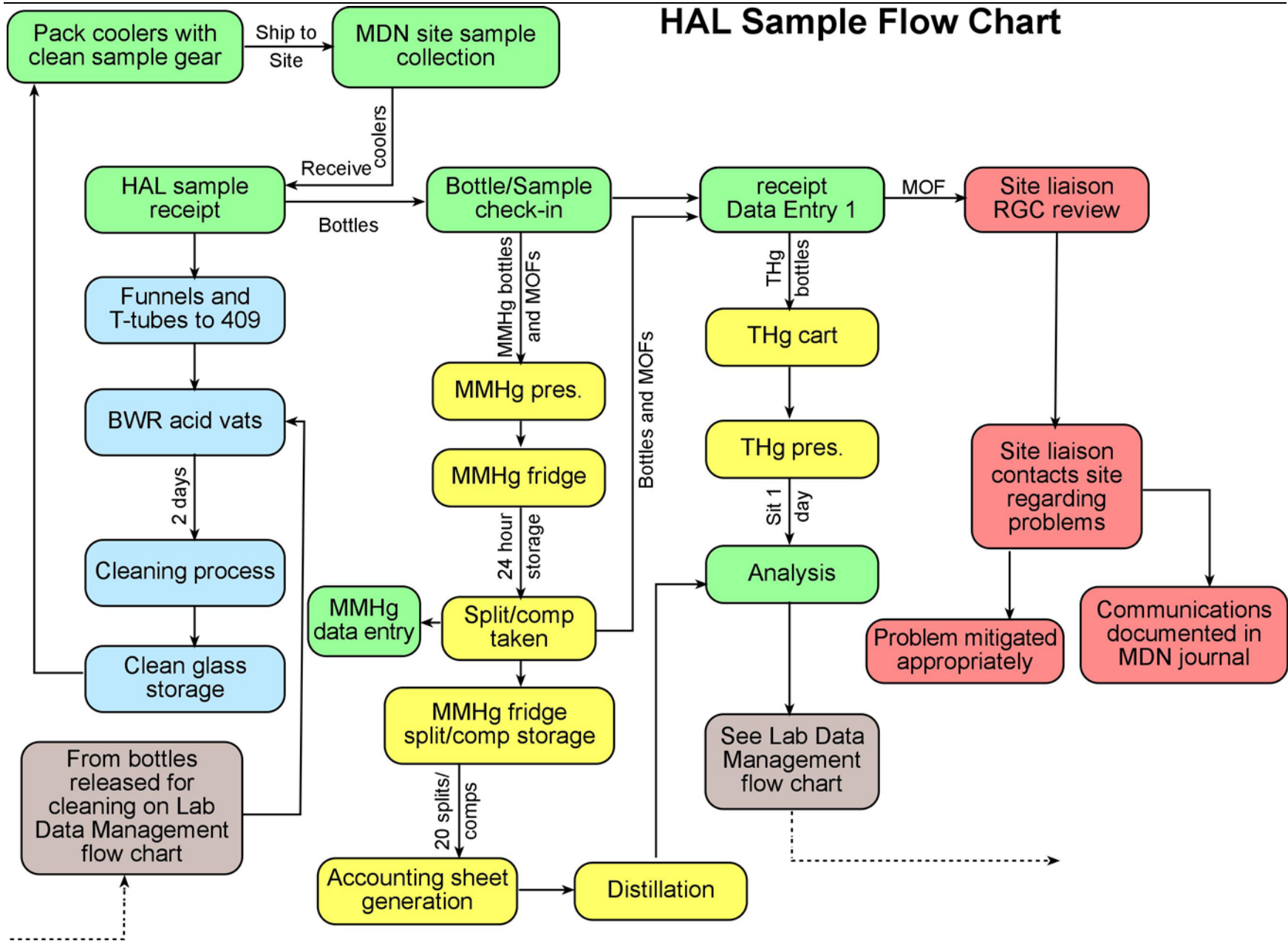


Figure 2: Sample analysis flow chart

# Lab Data Management Flow Chart

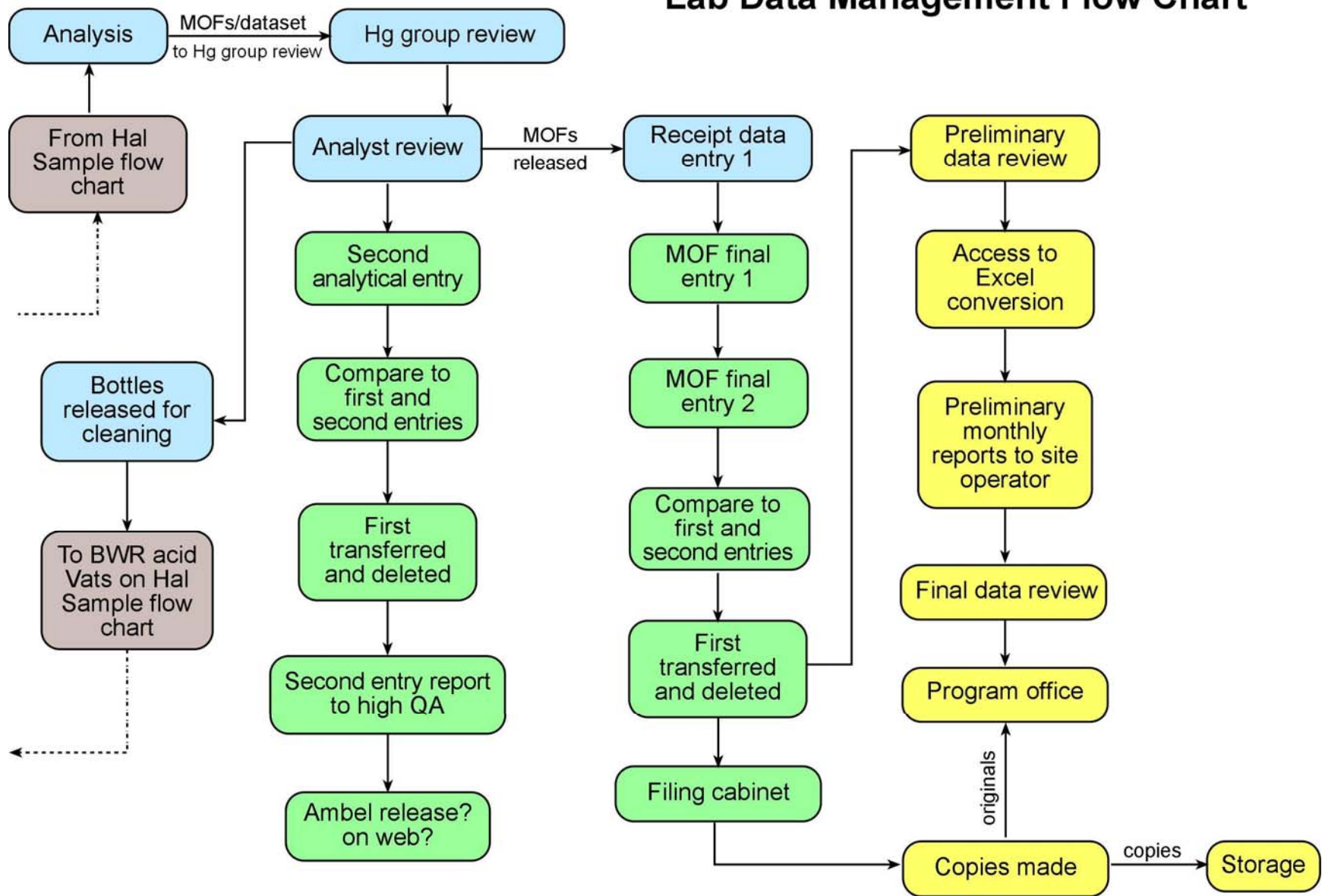


Figure 3: Lab Data Management Flowchart

## **5.2. Site Re-supply**

HAL supplies trace-level cleaned glassware to all MDN monitoring sites on a weekly basis. This glassware is shipped in specially padded coolers. The supplies provided by HAL are listed below:

- clean glassware, i.e. bottle, thistle tubes, and funnels
- clean unused dryside bag
- MOF and rain gauge charts when requested
- gloves
- Belfort ink
- lid seal pads
- insulation and air filters for MDN collector
- reagent water

The details regarding shipping and site re-supply are located in FGS MDN-10 Shipping.

## **5.3 MDN Site Liaison**

The Site Liaison has specific duties and responsibilities. Some of the Site Liaison's duties are listed below:

- provides communications between sites and HAL via e-mail, telephone calls, and faxes
- consults with individual sites about equipment use and malfunctions, siting regulations, and general network operations
- reviews each MOF for mention of equipment problems
- re-reads each rain gauge charts for verification/accuracy purposes
- documents all phone and e-mail correspondence in an electronic archiving system
- maintains the MDN-Network Equipment Depot (MDN-NED)





# **Section B:**

## **Field Operations**



## **1.0 Description**

This section presents a brief overview for defining and controlling the quality of sample collection and measurement activities at MDN precipitation collection sites. Further details are provided in QA documentation from the NADP Program Office (see <http://nadp.sws.uiuc.edu/lib/>). Included in these activities are the:

- selection and installation of monitoring locations, the collection of wet samples of atmospheric deposition
- maintenance of sample collection and measurement instrumentation
- quality control and quality coding of field measurements and observations
- instruction of site personnel in the standardized procedures used by the monitoring program

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). It is a modification of the Aerochem Metric collector (Aerochem Metrics, Inc., Bushnell, FL) and includes:

- 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)
- Teflon-wrapped sealing foam pads
- flexible sleeves at the base of the lid arms
- an enclosure around the collector base
- a thermostatically controlled heater and fan to minimize temperature extremes within the enclosure and to melt snow collected in the funnels

Precipitation samples accumulate in the wet-side bucket of the collector for one week and are removed each Tuesday at approximately 09:00 local time. The sample train is changed regardless of the sample volume. The exposed sampling train (bottle, funnel, and capillary tube) are removed from the sampler (the collection bottle is capped) and replaced with clean equipment received from HAL. When all required measurements have been made and all necessary observations have been recorded, the sampling train and completed standardized MOF are then shipped to HAL by second-day UPS or FedEx no later than the following business day.

Equipment is maintained and checked according to standard procedures specified in the Site Operation Instruction Manual (Welker, 1996). Replacement parts for sample collection equipment are furnished to sites on an as-need basis. Troubleshooting of all aspects of site operations is available through a Site Liaison located at HAL. A training video is also available for instructing site personnel in the procedures used by the network to collect, measure, and document mercury deposition samples.

## **2.0 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 Supervisor is not also the 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 a Site Liaison at HAL.

### **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 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. Site Sponsors are members of the NADP Technical Committee.

## **2.2 Site Supervisor**

Site Supervisors are responsible for overseeing site operations and for ensuring that sampling and network siting protocols are followed. Supervisors typically review the weekly data produced at the site, assist the Operator in troubleshooting operational problems, and work to make resources available to the Operator by coordinating with the agencies responsible for operation of the monitoring site. The Supervisor may or may not be the on-site or work supervisor of the Operator. The Supervisor may oversee operations at more than one site and is not required to be based nearby.

## **2.3 Site Operator**

The site Operator is the person primarily responsible for the day-to-day operation of the monitoring equipment; the weekly collection, on-site measurements, and submission of precipitation samples; and sample documentation. 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 Operator is also responsible for maintaining on-site records of site operations, including copies of the MOF, rain gauge charts, and memoranda concerning site operations, and the site operations manual.

## **2.4 Site Observer**

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

## **2.5 Technical Support of Collection Sites**

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

# MDN Equipment Flow Chart

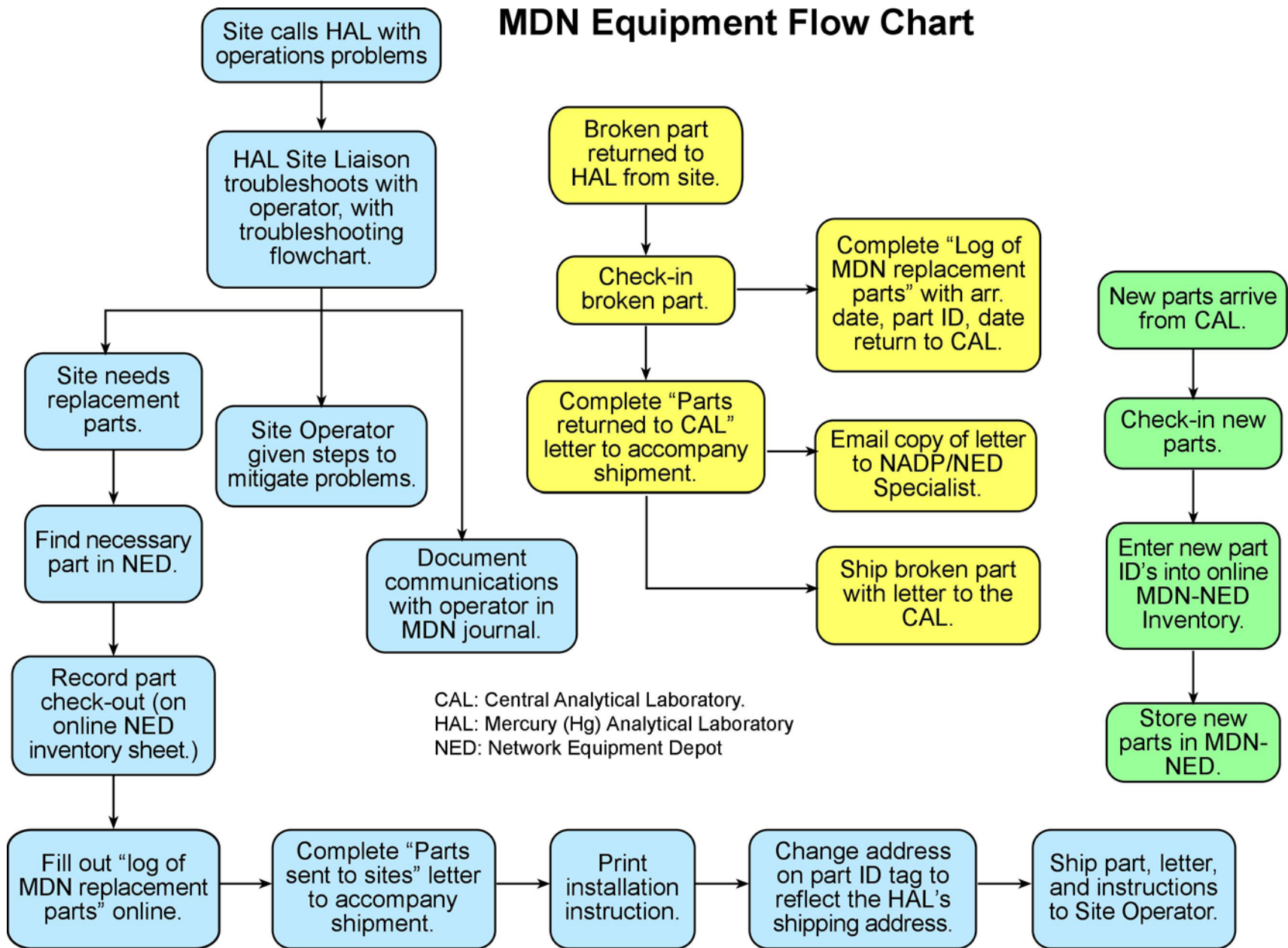


Figure 4: MDN Equipment Flowchart

### **3.0 Sample Collection**

MDN sample collection protocols currently include a Field SOP and a 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-slide lid. One train consists of acid-cleaned sample bottle, funnel, and thistle tube for mercury. The second auxiliary sample train may be used to collect duplicate samples, metal samples, or samples for other constituents. The modifications to the Aerochem Metric sampler are done at the NED in Champaign, IL and then shipped to the sites.

Approximately half of the MDN sites are at existing NADP/NTN sites. As with NADP/NTN, MDN is a weekly network where site Operators are instructed to visit their site each Tuesday at 09:00. A sample change is made regardless of the sample volume. The exposed sampling train (bottle, funnel, and capillary tube) is removed from the sampler (the collection bottle is capped) and replaced with clean equipment received each week from 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 FedEx no later than the following day.

Standard procedures for the handling of the mercury samples as well as for checking and maintaining the MDN collector are provided in a manual to all site operators (Van der Jagt, Brunette, 2006)

### **4.0 Record Keeping**

Information on the sample, the weather during the week, activities near the collector, and collector performance are recorded on the MOF. The MOF is a carbonless, triplicate, standardized form used to record field data. The top two sheets of the MOF and the rain gauge chart are sent to HAL with the weekly precipitation sample. For collocated MDN/NTN sites, a copy of the rain gauge chart is sent to HAL and the original chart is sent to CAL. 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 HAL.

### **5.0 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 the MDN site operations SOP.

Field QC will include: 1)Field Blank — a sample bottle with 20mL of 1% hydrochloric acid with the sampling train in place and left exposed for the entire sampling period without any collector openings. 2)System Blank — a Field System Blank is essentially a field blank in which a solution is poured through the wet side collection sample train that was installed in the field for an entire week with no precipitation. Currently the United States Geological Survey (USGS) supervises the MDN System Blank program.

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 collector compartment temperature will be verified by a max/min thermometer located within the encased bottom of the sampler on a weekly basis.

## **6.0 Performance and Systems Audits**

A collocated sampler program to estimate the variability of mercury measurements is in progress at WA18, IL11, VT99, and WI36. Duplicate MDN collectors collect field replicate samples at these sites. An independent contractor performs site audits.

## **7.0 Preventive Maintenance/Service**

### **7.1 Equipment Checks**

The site operation manual (Van der Jagt and Brunette, 2006) directs field personnel to practice preventive maintenance and to recognize the onset of possible equipment failures. The following maintenance procedures are conducted regularly:

- The collector sensor is cleaned every week 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 or not open soon enough.
- 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.
- The galvanized steel bucket in the rain gauge is replaced whenever excessive corrosion is noted.
- The foam lid seal on the precipitation collector is replaced when needed.
- The rain gage bucket is winterized with glycol for snow collection in the Fall, and the glycol is removed in the Spring

### **7.2 MDN Network Equipment Depot (NED)**

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 lost of operational time that results from equipment failures. The Site Liaison at 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.

## **8.0 Corrective Action**

The MDN Site Operations Manual lists 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:

- If the Operator notes out-of-tolerance behavior for the equipment, the Operator attempts to correct the problem and makes a notation on the next MOF along with an estimate of the amount of time the equipment was affected by the out-of-tolerance condition. If the problem cannot be corrected, the operator contacts the site liaison at HAL for assistance in correcting the problem.
- If the need for corrective action is noted at HAL or the NADP Program Office while reviewing the information submitted from a site, the Operator is alerted via telephone or e-mail to initiate 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 by the MDN Coordinator with assistance from the NADP QA Manager.

## **9.0 Reporting And Documentation**

Results of the site QA/QC activities will be compiled in several types of reports that are distributed to MDN Sponsors, network management, and to the 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 database.

- Monthly HAL preliminary data printouts are sent to each site Operator, Sponsor, and the NADP Program Office.
- A report titled *Quality Assurance Report: MDN Deposition, Monitoring, and Field Operations* will be prepared periodically by the QA officer. It will summarize QA aspects of field operations and be distributed to NADP members.



# **Section C: Laboratory Operations**



## **1. Laboratory Procedures**

### **1.1. Documentation**

FGS's goal is to be able to trace all laboratory measurements to their sources and to operate within specified measurement quality objectives. The laboratory uses traceable reagents, standards, and reference materials in all procedures. Furthermore, all standard solutions and analytical reagents are tested for suitability before use. All testing is documented. The documentation is traceable within LIMS..

All calibrations are traceable to certified standards or manufacturer lot numbers. For analytical instruments, high purity calibration standards are obtained from chemical suppliers. Certificates attesting to the concentration ranges of the applicable analytes are retained in the QA Office. Each certificate is labeled with the date received, the staff member's initials, and a unique laboratory ID number. All raw data references the unique laboratory ID number for each calibration standard. This number can then be traced through LIMS to the original shipment, bottle, certificate, or lot number.

The performance of analytical support equipment (e.g. balances, pH meters, pipettes, refrigerators, ovens) is routinely verified by FGS staff. In addition, all analytical support equipment is calibrated or verified by a certified metrology laboratory at least once per year. When support equipment is checked or calibrated, measurements are recorded in laboratory logbooks or in the calibration file in the QA Office. The calibration tolerances of the analytical support equipment are listed in their respective SOPs (FGS-002, FGS-003, FGS-004).

### **1.2. Reagents**

Analytical reagents are tested whenever a new lot arrives from the manufacturer, to ensure they meet specifications documented in the appropriate SOP. Upon approval, quantities of the reagent are purchased and sequestered at the laboratory. Test results are kept by the applicable Group Leader(s).

Additionally, reagents undergo continuous monitoring through analysis of method blanks. A method blank is a sample of reagent water and analytical reagents that undergoes the same analytical process as the corresponding samples. A minimum of three method blank samples are prepared with each analytical batch. For MDN, a typical analytical batch consists of 30 samples.

### **1.3. Standards**

Stock standards are logged into LIMS upon receipt or when prepared, and are given a unique identification number. Original documentation is labeled with receipt date and receiver's initials and given to the QA Office. The QA Office is responsible for maintaining standard records as well as updating folders where copies are kept. All raw data references a unique laboratory ID number for calibration standards. This ID may then be traced through the standards logbooks to the original shipment, bottle, and certificate or lot number. Procedures for standards documentation are detailed in FGS-074 Stock and Working Standards for Trace Metals Analysis, FGS-069 Total Mercury Analysis by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS), and FGS-070 Methyl Mercury Working Standards and Instrument Calibration.

All freshly prepared standards and purchased standards are logged into the Laboratory Information Management System (LIMS) and are given a unique identification number. The identification number indicates the year in which the standard was received or created, and the order in which it was entered into LIMS. For example, the first standard entered into the LIMS system for 2006 is identified as 0600001, the second 0600002, etc. All parent standards used in the creation of new standards are documented within LIMS. The date received, or the date created, and preparer's initials are noted on the standard and on the certification information shipped with the standard.

## **1.4. Certified Reference Materials:**

Where possible, FGS uses reference materials that are certified and traceable to national or international standards of measurement. Certified reference materials are logged into LIMS when received, opened, and disposed of. The date of receipt (with initials) and date opened (with initials) are written on the bottle as well. Certificates of analysis are given to the QA Office. Certificates of analysis indicate date of receipt, and the receiver's initials. The QA Office maintains a file of the original certificates of analysis in a three-ring binder. Additional copies of the certificates are provided to the laboratory staff for reference.

## **1.5. Calibration of Analytical Instruments:**

Every instrument used to analyze samples at FGS must pass the calibration criteria in the relevant SOP. Initial calibration criteria for instrument reproducibility and sensitivity must be met before samples may be analyzed. Continuing calibration checks establish whether ongoing instrument calibration is acceptable. Procedures for instrument calibration are detailed in FGS-069 Total Mercury Analysis by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS) and FGS-070 Methyl Mercury Working Standards and Instrument Calibration.

Due to the variety of methods and instruments used at FGS, individual SOP must be referenced for specific calibration protocols. In general, calibrations start with a linear five-point curve forced through zero. Correlation coefficients are generally required to have an "r<sup>2</sup>" value greater than or equal to 0.990.

## **1.6. Calibration Verification for Analytical Instruments:**

All standard solutions are traceable to certified standards or manufacturer lot number. An initial calibration verification (ICV) standard is analyzed following each calibration curve to verify the accuracy of the calibration. The ICV is a standard solution made from a traceable second source, independent of the source used in the calibration standard solution. A continuing calibration verification (CCV) standard verifies that the analytical system is in control or demonstrates analytical drift. The CCV is a standard solution that is made from a traceable stock standard (usually the same as the calibration stock). CCV are generally analyzed at a frequency of one per every ten samples and another at the end of each analysis. All raw data references a unique laboratory ID number for each standard used in the analysis. This ID can then be traced through the standards logbooks to the original shipment, bottle, and certificate or lot number.

## **2. Sample analysis**

### **2.1. Laboratory Quality Control Samples**

The laboratory uses quality control (QC) samples to assess the validity of analytical results. QC samples include instrument blanks, preparation blanks, initial and continuing calibration verification standards, initial and continuing calibration blanks, reference materials, duplicates, and spiked samples. QC samples are analyzed the same as field samples, at a frequency described either in this QAP or the applicable SOP. If the QC sample results fall within the acceptance criteria (also detailed in the method, this QAP, or SOP), then the analytical data is considered to be valid or acceptable.

### **2.2. Laboratory Bottle Blanks**

#### **2.2.1. Description**

Following cleaning, HAL bottles are charged with 20mL of 1% hydrochloric acid. Two random bottles are then analyzed for total mercury each week.

### **2.2.2. Purpose**

Even in an ultra-clean laboratory, mercury exposure is inherent to the handling of MDN sample bottles. Because such contamination is inevitable, it must be analyzed and quantified so that it can be subtracted from final sample results, objectively.

## **2.3. Preparation Blanks**

### **2.3.1. Description**

Preparation Blanks for total mercury consist of 1% (v/v) 0.2N bromine monochloride, 0.2mL 20% hydroxylamine hydrochloride, and 0.3mL 20% stannous chloride in 100mL of reagent water. Preparation blanks for methylmercury consist of hydrochloric acid, APDC solution, ethylating agent, acetate buffer, and reagent water.

### **2.3.2. Purpose**

Mercury content is inherent even in FGS' preparatory and analytical reagents. Preparation Blanks are a measure of how much of each sample result can be attributed to these necessary reagents and also help when investigating possible sources of contamination.

## **2.4. Ongoing Calibration Standards**

### **2.4.1. Description**

Ongoing Calibration Standards are continuously analyzed during the course of sample analysis, typically after a suite of ten samples and at the end of each analytical day. A 1.0ng standard for total mercury and a 0.1ng standard for methylmercury are typically analyzed as an Ongoing Calibration Standard.

### **2.4.2. Purpose**

Ongoing Calibration Standards verify that the analytical system is in control. All total mercury standard solutions are traceable to certified standards or manufacturer lot number. Currently there is no commercially available methylmercury standard. All raw data references a unique laboratory ID number for associated standards. This ID may then be traced through LIMS to the original shipment, container, and certification. The acceptance criteria for ongoing calibration standards is 75-125% recovery.

## **2.5. Ongoing Calibration Blanks**

### **2.5.1. Description**

Ongoing Calibration Blanks are continuously analyzed during the course of sample analysis, typically after a suite of ten samples and at the end of each analytical day.

### **2.5.2. Purpose**

Instrument blanks are used to demonstrate freedom from system contamination, carryover, and to monitor baseline drift.

## **2.6. Matrix Duplicates**

### **2.6.1. Description**

Matrix Duplicates are created when an existing sample is split into two portions that can then be compared analytically.

### **2.6.2. Purpose**

As there is no theoretical difference between a pair of matrix duplicates, their relative percent difference (RPD) is expected to be less than 25%. Out of control results are indicative of a heterogeneous sample matrix and/or poor analytical precision.

## **2.7. Matrix Spikes**

### **2.7.1. Description**

A Matrix Spike is created when an MDN sample with known mercury content is supplemented with an additional 1.00ng of mercury standard.

### **2.7.2. Purpose**

As the combined mercury content of the Matrix Spike sample is known in theory, matrix spike recoveries are expected to be within 75-125% of this theoretical value. Matrix Spike recoveries determine if, and how, the sample matrix interferes with target analyte recovery. They also ensure that HAL's preparation and analytical procedures do not result in significant analyte loss.

## **2.8. Certified Reference Materials**

### **2.8.1. Description**

Certified Reference Materials are commercially available samples containing known quantities of analyte in a specific matrix. Currently, there is no available Reference Material matching the MDN rainwater matrix. Instead, HAL uses National Institute of Standards and Technology Reference Material 1641d – Total Mercury in Water. For methylmercury, HAL uses National Research Council Canada Reference Material DORM-2.

### **2.8.2. Purpose**

Certified Reference Materials are used to demonstrate HAL's ability to recover a target analyte from a specific matrix. They are also a secondary source for verifying the validity of the analytical curve. The acceptance criteria for certified reference materials is 75-125% recovery.

## **2.9. Blank Spikes:**

### **2.9.1. Description:**

A Blank Spike is a sample of reagent water or analytical reagents that has predetermined quantities of analyte added. It undergoes the same preparation and analytical processes as the corresponding samples.

### **2.9.2. Purpose**

Blank Spikes are used to evaluate the daily performance of a method, but are not subject to matrix effects that may occur in matrix spikes. They are used primarily when no appropriate reference material is available for a particular matrix.

## **2.10. Method Detection Limits**

Method detection limit (MDL) studies are maintained for all matrix/analyte combinations available at FGS. Studies are performed using the protocols in 40 CFR, Section 136, Appendix B. Specifically, seven or more low-level matrix-specific spikes are processed according to preparation and analytical method protocols. The MDL is determined as  $t^*SD$  of the replicates (where  $t$  is the Student's T-value for the number of replicates minus one degree of freedom, and SD is the standard deviation). FGS updates MDL studies in response to method revisions or client request.

## **2.11. Reporting Limits**

FGS has also developed reporting limits that are based on MDL study results, as well as results from low-level spikes that were performed with each sample batch over a nine-month period. In this way, reporting limits reflect the variability associated with multiple analysts running multiple instruments over an extended period of time. Reporting limits are supported by ongoing MDL studies and are re-assessed periodically.

## **2.12. Control Charts**

FGS's database allows most QC results to be collected instantaneously in the form of control charts. Control charts allow the MDN Project Manager and laboratory staff to spot unfavorable analytical trends as they are developing. Corrective actions for those trends can in turn be assessed in real time. Additionally, control charts are periodically used in the calculation of efficiency factors for certain distillation and precipitation methods. Finally, control charts are the basis for FGS's Facilities Monitoring.

## **3. Performance and System Audits**

### **3.1. Internal Laboratory Audits**

On a quarterly basis, FGS's QA Office under the supervision of the QA Officer conducts an internal laboratory audit according to the procedures in FGS-041 Internal Quality Assurance Audits. The QA Office writes an audit report with observations and findings. The MDN Project Manager, working closely with the senior laboratory staff, has two weeks to provide a written response to the report detailing corrective actions and implementation dates. If the QA Officer accepts the response, the audit report and response are validated and are included in the next QA Program Quarterly Report. The QA Office maintains a file of past internal audit reports.

### **3.2. External Laboratory Audits**

FGS views third-party audits as a form of consultation and welcomes the opportunity to improve the quality of our lab. On average, FGS is audited approximately four times each year. External audits enable FGS to qualify for and maintain accreditation through state governments and NELAP. Additionally, clients may audit as part of a potential or ongoing contract. The QA Office maintains records of all such audits, their findings, and their corrective actions. Currently HAL is audited by the NADP office once every three years. HAL is considered part of FGS's general laboratory and thus participates in other external audits.

## **4. Corrective Action**

### **4.1. Deviation from Laboratory Policy**

There are times in the course of analytical laboratory work when it is necessary to depart from strict adherence to a particular policy. Within the context of FGS's requirement that all staff work in a manner consistent with its QA program, FGS fosters a creative environment. FGS's staff is instructed to never compromise data quality or safety for the sake of compliance. However, such departures must be documented appropriately, and all stakeholders must be informed. Reasons for a departure from written policy may include safety concerns, data quality, research and development, acts of nature (e.g., storms, power outages), matrix interference, and instrument performance.

FGS-087 Procedures for Deviation from Laboratory Policy details the procedures for intentional deviation from policy. Corrective actions may include filing an incident report, revising an SOP, revising the QAP, revising a safety procedure, or writing a new SOP.

## **4.2. Incident Reports**

Mistakes and accidents occur in the course of analytical laboratory work. These must be immediately reported to the supervisor and documented on an Incident Report Form. If there are safety concerns, a report is also filed with the Health & Safety Officer.

An Incident Report Form is completed when a problem arises that requires a deviation from the applicable SOP or method. The deviation may be due to a mistake or accident. It also may be due to unforeseen problems with a sample, instrument, or dataset. Whatever the circumstance, it must be recorded as soon as possible according to FGS-039 Incident Report Forms. It is the responsibility of each Group Leader (or delegate) to complete Incident Report Forms and submit them to the QA group for review and follow-up. Completed Incident Report Forms are kept on file in the QA group and are assessed quarterly as part of each internal audit. They are also routinely submitted to the Management Committee as part of the QA Program Quarterly Report.



# **Section D: Data Management Operations**



# 1. Preventive Maintenance/Service

FGS employs seven servers, all running Windows Server 2003 in an Active Directory environment. Two of the seven servers act as domain controllers to control and maintain security access and access policies using the NTFS file system. Separate servers are utilized to control remote access to the network, terminal services, file and print services as well the company Exchange 2003 email server. In addition to the Windows 2003 servers FGS employs one additional server running VMWare ESX Server 3.5.1. All servers are equipped with backup drives and appropriate backup software that provides scheduling, automation, and monitoring of back-ups.

The server room is located in a cement-lined vault with a 6-inch thick metal door. It is closed each evening according to the lab lockup procedure to protect against fire. There is a facility-wide security system with motion detection that is activated each evening, also according to the lockup procedure to protect against theft. The servers and other network hardware are installed at least three inches above the floor to protect from water damage.

Each server is attached to a UPS system with monitoring software and has enough battery power to keep the server running for at least twenty minutes. If the power is out for more than five minutes, the software will shut down the server automatically storing all data before battery power runs out. Network devices such as routers, switches, and hubs are also attached to a UPS device. All other FGS computers also have some form of UPS to minimize data loss, and loss of instrument control due to a short power failure. The servers, network hardware, and all other FGS computers' AC power supplies are plugged into power strips with built-in surge/spike protection.

Norton Anti-Virus (NAV) software with immediate file protection services is installed on each server. Files on the server disks are scanned daily. Virus definitions are updated automatically each day via an Internet connection to the software vendor. NAV for Exchange is installed on the mail server to scan incoming and outgoing mail attachments for viruses. Attachments with the file extensions ".exe", ".pif", ".bat", ".vbs", and ".scr" are deleted from all e-mails that are sent to FGS. E-mail alerts are sent to IT personnel upon detection of viruses or unauthorized attachments. If FGS gets a large number of bad attachments in a day, the Internet mail service may be shut down until the problems are rectified. NAV is also installed on each employee's computer to protect against infected files brought in through the Internet, outside e-mail accounts, or portable diskettes, and flashdrives.

Access to computers and files is limited to domain users with passwords that grant access to job-specific files and folders using the file securities built into the file system. Data security has been divided into three categories: access, protection against corruption, and redundancy. Access to data is subject to levels of control. The data owner determines data criticality. Non-critical data is available throughout the network. Critical data is available to members of predefined groups only. Sensitive and proprietary data is restricted at the user level. Data is protected from corruption by a strategy of limited access and redundancy. Redundancy takes the form of data backups via computer and secure storage of data in hard copy. Backups cover the primary domain controller, the backup domain controller, and individual workstations.

## 2. Data Management Operations

### 2.1. Description

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

Data records from MDN monitoring sites, and the HAL are transferred to the NADP Program Office. This data is a mixture of primary data records, summaries of primary data, and results of

data-quality evaluations that were performed as routine QC. The records may include paper or hardcopy documents as well as electronic documents.

## **2.2. MDN Monitoring Sites**

Each site submits a weekly MOF that contains information about the sample submitted to HAL. This information includes a definition of the sampling period, a report on the sample condition, precipitation information, and site operations information. The MOF is accompanied by a recording rain gauge chart. The site operator is responsible for submitting data to HAL. The operator is also responsible for remedying incomplete or inaccurate site data.

## **2.3. The Mercury Analytical Laboratory**

HAL is the main technical contact point for MDN monitoring sites and is the only laboratory conducting the chemical analysis of the network samples. 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, HAL is responsible for the initial assessment of data quality.

The MDN Project Manager has overall responsibility for the laboratory's MDN data management activities. The MDN Site Liaison has responsibility for information exchange between 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 the QA Officer. The MDN Project Manager is responsible for all additions, deletions, and updates to the MDN data.

## **3. Objectives And Goals**

Achievement of the overall objectives of the MDN monitoring program is largely dependent upon 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.

### **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. Data completeness affects the accuracy and representativeness of calculated annual atmospheric deposition at a site.

### **3.2. 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:

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

Data review and validation ensures that raw data is properly reduced and accurately transcribed to the correct reporting format. FGS-038 Data Validation is referenced for data reduction and review. After the data has been acquired, data reduction is performed using validated spreadsheets and databases that automate calculations as much as possible. Initial data review

is performed by the analyst. The data is then submitted to Mercury group for peer-review. Peer-review consists of validating at least 5% of the calculations and 100% of the following:

- transfer of raw data from the digestion sheet or bench sheet to the electronic spreadsheet
- project name
- data set ID
- sample identities
- peak heights/areas
- instrument calibration
- all QC samples (e.g. blanks, SRM, CCV, MD, MS and MSD, BS)
- detection and reporting limits
- compliance with the individual method
- QC sample results must be reviewed for accuracy and precision as established by FGS and/or client specifications
- documentation of corrective actions and outliers

If the data meets all FGS and contract-mandated QC requirements, the raw data is stamped "Quality Assurance Peer-Reviewed" with the reviewer's initials and the date. All MDN datasets go through HIGH QA review before it gets released to the MDN project manager.

### **3.3. Documentation**

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

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

### **3.4. Data Reporting**

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

- Site Operators submit standard field documentation to HAL within 48 hours after removing the sample from the field.
- Site Operators receive a preliminary report of field data and laboratory chemical analysis results monthly.
- Site Operators are requested to fill in a preliminary data review form and submit the report to HAL, even if no corrections need to be made.
- HAL transfers all required final data and supporting documentation, on monthly basis, to the NADP Program Office within 90 days of the end of the respective month.
- Quality assured data from each site are available to the public within one year of field sampling.
- Special data reports and summaries adhere to the same data-quality requirements as routinely scheduled network data reports.

## **4. Data collection, entry and transfer**

### **4.1. Weekly Field Information**

The NADP/MDN Site Operation Instruction Manual contains the Operator's instructions for completing the weekly MOF and for interpreting the weekly rain gauge chart. When completed, this information is forwarded to HAL by the Operator each week.

At HAL, each MOF and rain gauge chart is coded with a unique, alpha-numeric laboratory identification (HAL code). 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. All MOF data is double data entered. The two separate entries are compared to ensure accurate data entry.

### **4.2. Chemical Analysis Results**

The analytical results are also double data entered into the MDN database. 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, on a monthly basis, within 90 days of the end of the respective month to the Program Office. In both automated and manual data acquisition, laboratory analysts are responsible for the correct entry and transformation of instrumentation output.

## **5. Data Verification And Validation**

### **5.1. Weekly Field Information**

Immediately after the data from the MOF is entered into the EMOF, the MDN 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 if necessary. A validation code, known as a sample note code, is automatically assigned to each deposition sample to indicate departures from standard sample collection procedures that may have compromised sample integrity. There are several manual codes that could be assigned to samples on a case-by-case basis. For detailed descriptions please refer to MDN-15. The MDN Site Liaison maintains, for reference and documentation purposes, a record of all oral and written communications with site personnel.

### **5.2. HAL Preliminary Data Reports**

HAL sends the site Operator and Sponsor a monthly report that contains preliminary results of HAL's chemical analysis and information contained on the MOF, along with comments concerning errors or potential problems at the site. Operators are asked to respond to any deficiencies noted on the preliminary reports and to verify the MOF information contained therein. Any other information regarding data quality resulting from this review is forwarded to HAL. Responses are made by annotating the appropriate report page and mailing it back to HAL in the shipping container during the next regularly scheduled sample submission. The MDN Project Manager reviews the responses and makes the necessary changes if applicable after verification.

### **5.3. Merged Field and Chemical Analysis Data**

The MDN Site Liaison receives the MOF, rain gauge charts, and all other accumulated information relevant to the validation of site records. Note codes are automatically assigned by the DBMS to samples that were contaminated or that were identified as having been handled in a manner inconsistent with field or laboratory protocols. Note codes can be assigned manually based on the MDN Site Liaison's review of MOF, rain gauge charts, and correspondence with the Operator. After this review, the MOF information and the analytical data are merged 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 Database Manager.

### **5.3 Data Modification**

The MDN Project Manager makes all the changes in the MDN database. All changes are documented on the respective MOF or laboratory datasheets. When appropriate, data modifications are also documented in the MDN database.

## **6. Record Keeping**

### **6.1. Network Data**

Forms that originate at field sites (MOF and rain gauge charts) are archived at the Program Office for the life of the MDN project. Other site records that originate at HAL, such as transcripts of communications and other correspondence, are attached to the second of the three-part MOF and archived at HAL. Results of the 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 HAL. All records are archived for the life of the project.

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 HAL and the Program Office are stored for the life of the project. At HAL both paper and electronic records are kept under the supervision of the MDN Project Manager. At the Program Office, MDN records are maintained under the supervision of the MDN Coordinator.

### **6.2. Quality Assurance Reporting**

At least quarterly, the MDN Project Manager reviews any changes in the chemical analysis of samples or data management activities at 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.

# Frontier GeoSciences – MDN Specific SOPs

MDN - 01 - Field SOP
MDN - 02 - Sample Receipt Procedures
MDN - 03 - Data Entry
MDN - 04 - Total Mercury Preservation
MDN - 05 - Total Mercury Analysis
MDN – 06 - Methyl Mercury Preservation, Splits and Comps
MDN – 07 - Distillation of MDN Precipitation Samples for Methyl Mercury Analysis
MDN – 08 - MDN Methyl Mercury Analysis
MDN – 09 - Cleaning of MDN Sampling Glassware
MDN – 10 - Shipping of MDN Sampling Glassware
MDN – 11 - Interpretation of the Rain Gauge and Event Recorder Chart
MDN – 12 - MDN Data Review and Validation
MDN – 13 - MDN Journal Procedures
MDN – 14 - Pipette Calibration and Maintenance
MDN – 15 - MDN Monthly Review and Sample Coding

**Figure 5: MDN Specific SOP List**



# Frontier GeoSciences – Supplemental SOPs

FGS-002 Balance Calibration and Maintenance
FGS-004 Refrigerator and Freezer Calibration and Maintenance
FGS-007 Cleaning of Sampling Equipment and Bottles for Mercury Analysis
FGS-039 Incident Report File
FGS-048 Creation and Control of Standard Operating Procedures
FGS-061 Gold Trap Construction
FGS-062 Preparation of Carbo-Traps for Methyl Mercury Analysis
FGS-067 Passive Diffusion Monitoring for Gas Phase Atmospheric Mercury
FGS-072 Ordering Laboratory Supplies
FGS-074 Stock and Working Standards for Trace Metals Analysis
FGS-086 Documentation of Equipment Maintenance
FGS-087 Procedures for Deviation from Laboratory Policy
FGS-089 Sputter Coating Quartz Sand
FGS-087 Procedures for Deviation from Laboratory Policy
FGS-089 Sputter Coating Quartz Sand
FGS-099 Waste Dumping Procedure for Client Sample Waste
FGS-101 Traceability Protocols
FGS- 041 Internal Quality Assurance Audit

**Figure 6: Supplemental SOP List**