Laboratory Quality Assurance Plan

National Atmospheric Deposition Program
Mercury and Central Analytical Laboratories

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465 Henry Mall
Madison, WI 53706

Analytical Laboratory Address:
2601 Agriculture Drive
Madison, WI 53718

University of Wisconsin-Madison
Wisconsin State Laboratory of Hygiene

Website: http://nadp.slh.wisc.edu/

Revision 1 – June 25, 2020

National Atmospheric Deposition Program

1 Applicability

1.1 NADP Sponsors

This Quality Assurance Plan (QAP) is designed to meet the needs of the National Atmospheric Deposition Program (NADP) and is modeled after quality assurance requirements of the National Environmental Laboratory Accreditation Program (NELAP), the Wisconsin Department of Natural Resources Lab Accreditation Code (NR 149), and the Environmental Protection Agency (EPA) Safe Drinking Water Lab Accreditation program. The NADP is structured as a cooperative program that represents coordinated efforts of many individuals in federal, state, tribal, academic, and private organizations to operate monitoring sites, generate/report data, and oversee research activities related to atmospheric chemistry and wet and dry deposition.

There are multiple monitoring networks within NADP each with unique monitoring infrastructure, sample collection protocols and data quality objectives. However, as components of NADP, these networks all support the NADP mission of exceptional data quality, outreach, and scientific improvement. The NADP Program Office (PO) manages the operations of NADP, oversees activities of all the networks and works closely with the network laboratories to publish the environmental monitoring data. The Central Analytical Lab (CAL) and the Mercury (Hg) analytical lab (HAL) through close coordination with the PO, aim to fulfill the mission of NADP as described in the Governance Document and as directed by the Executive Committee. Any opinions, findings, conclusions, or recommendations expressed in this plan are those of the authors and do not necessarily reflect the views of the sponsors. This laboratory QAP is approved by the Program Office and the Quality Assurance Advisory Group (QAAG).

1.2 CAL and HAL Historical Perspective

The Wisconsin State Laboratory of Hygiene (WSLH), located in Madison WI, operates as a unit of the University of Wisconsin – Madison's School of Medicine and Public Health (SMPH) and has been Wisconsin's public, environmental and occupational health laboratory since 1903. As part of a land-grant university, the WSLH/NADP can preferentially access Hatch Act research funds through its State Agricultural Experiment Station (SAES). The WSLH is also the statute-designated analytical lab for the WI Department of Natural Resources (WDNR) and WI Department of Health Services (WDHS). The lab's mission is to improve and protect the human condition by providing accurate and precise testing, service, research and education. The WSLH accomplishes its mission through the implementation of advanced analytical techniques in environmental assessment and public health studies.

The WSLH took on the responsibility and role of the NADP CAL on June 1, 2018, after a short transition period from the Illinois State Water Survey (ISWS) located at the University of Illinois in Urbana-Champaign, Illinois. The NADP PO, was also formerly located at ISWS and transitioned to the WSLH in March of 2018.

When the WSLH became responsible for the program there were four national networks and one initiative (potential future formal network) under the umbrella of NADP that required laboratory support. These networks are: National Trends Network (NTN), Ammonia Monitoring Network (AMoN), Atmospheric Integrated Research Monitoring Network (AIRMoN) and the Mercury

Deposition Network (MDN). The initiative is called Mercury Litterfall Monitoring. These networks and the support laboratories must follow strict quality assurance (QA) and quality control (QC) procedures. See Table 1 for a Network Summary.

The NADP CAL provides site supply services, sample processing, chemical analysis, precipitation review and data validation services for precipitation samples collected by the NADP NTN, and passive air samplers for the NADP AMoN. The ISWS CAL analyzed NTN samples from the network's inception in 1978 until May 31, 2018; AIRMoN samples from 1992 to May 31, 2018; and AMoN samples from 2007 to May 31, 2018. WSLH began support and analysis for those networks on June 1, 2018. AMoN and NTN are ongoing networks, while AIRMoN ended operations in September of 2019.

The WSLH took ownership of the HAL on June 1, 2019 from Eurofins Frontier Global Sciences (EFGS) located in Seattle, WA. The NADP HAL is responsible for site supply services, sample processing, analysis, and data validation for the Mercury Deposition Network (MDN). The HAL is also now responsible for the Mercury Litterfall Monitoring initiative. The EFGS HAL analyzed NADP/MDN samples from 1996 through May 31, 2019. The Litterfall initiative was implemented entirely as a USGS network until the fall of 2019 when the WSLH took over sample processing and chemical analysis. The WSLH/NADP will assume responsibility for field support of the Litterfall Monitoring initiative in late summer 2020.

Due to the fact that the CAL and HAL are all housed within WSLH we are using many overarching QA goals/tools and assessments to address lab functions. This provides many efficiencies and enables better consistency among networks.

Table 1. NADP Network Summary

Network	Number of Sites (2020)	Sampling Frequency	Matrix	Analytes	Preservation
NTN	259	Weekly	Precipitation	pH, Conductivity, Ca, Mg, Na, K, Cl, NO_3, SO_4, NH_4, PO_4	Refrigerate after Receipt
AMoN	110	Biweekly	Air	NH_4 (calculated NH_3)	Freeze after Receipt
AIRMoN	0	Event Based	Precipitation	pH, Cond, Ca, Mg, Na, K, Cl, NO_3, SO_4, NH_4, PO_4	Shipped Iced, Refrigerate after Receipt
MDN	85	Weekly	Precipitation	Total Hg, Methyl Hg	1% HCl at collection

1.3 Program Objectives

The primary program objectives of the CAL and HAL are (a) preparation and provisioning of all supplies (buckets, bottles, sample trains, passive samplers, etc.) for all network sites, (b) chemical analysis of wet deposition and atmospheric passive samples, (c) data review/verification (d) data reporting to the PO (e) maintaining the CAL archive samples, (f) continuous network data improvement, and importantly (g) implementation of a robust QA program.

Although this document addresses current NADP programs, new initiatives are periodically introduced within NADP resulting in new programs for the CAL and/or HAL. When new initiatives transition to approved programs, any procedures for ensuring quality data of these new programs will be documented

in Standard Operating Procedures (SOPs), with general information added to the QAP as needed. There are many supporting documents linked within this QAP. The supporting documents are not open access, however the CAL or HAL can supply copies of any of the referenced documents upon request. Many supporting documents can also be found in the Appendices. This QAP also contains a large number of acronyms – refer to **Appendix K** for a table of acronyms.

1.4 Quality System Objectives

The CAL and HAL's quality systems ensure data are of sufficient quality to reliably estimate spatial variation and temporal trends in atmospheric wet-deposition, and that measurements of data quality are well documented and communicated. The management and laboratory professionals are committed to following good professional practices as defined by the quality system. It is the responsibility of all lab staff to follow appropriate QA/QC practices. Any significant changes to the supplies, sample handling or analytical procedures are thoroughly tested, approved as applicable and the date of change is tracked in this table: O:\Teams\NADP\NADP Lab\Major Changes\NADP CAL HAL Major Changes.xlsx.

1.4.1 Data Integrity

All management and laboratory professionals are committed to ethical laboratory practices. All employees are responsible for following the WSLH data integrity, ethics, and data documentation policies.

1.4.2 Continuous Quality Improvement

Laboratory management and staff are dedicated to continuous quality improvement by means such as corrective and preventive action when warranted, root cause analysis, internal audits, and management system reviews. Staff members are encouraged to bring suggestions to management for quality improvement consideration. Staff are also encouraged to seek and take advantage of professional advancement opportunities.

1.4.3 Customer Satisfaction

The laboratory's standard of service to all of its customers includes meeting all quality system objectives, providing timely results, remaining fiscally responsible, and addressing customer questions and concerns. Research and method development may also be requested and pursued as resources allow.

1.4.4 Staff Training

Training includes initial and continuing instruction on the quality system documented in this QAP and referenced policies and procedures as required for specific job duties (See Section 2.11). Training ensures that the quality system is communicated, understood and implemented by appropriate personnel.

2 Organization, Management Structure, and Responsibilities

2.1 WSLH Overview

The WSLH is an operating unit of the School of Medicine and Public Health at the University of Wisconsin (UW) – Madison, in Madison WI. The WSLH was established by state statute in 1903 and is overseen by the 11-member WSLH Board. The Board serves to set policy and direction for the Laboratory, and its members are either designated by state statute (e.g. representatives of several state

agencies) or appointed by the Governor of Wisconsin. Operational management of the WSLH is the responsibility of the Laboratory Director. The WSLH follows the policies and procedures established at the UW. The NADP CAL/HAL operate under the Environmental Health Division (EHD) within the WSLH.

2.2 Divisions

The WSLH organization is composed of several operating divisions including the Environmental Health Division. See O:\Organizational Charts for the most recent WSLH organizational charts. The current labwide and EHD charts are included in **Appendix A**. There are approximately 110 staff currently in the EHD with roughly (depending on staffing levels/vacancies) 16 associated with the NADP CAL/HAL. The EHD has a robust overarching QA program that this QAP follows. There is also a Labwide Quality Assurance Committee (QAC) that functions to provide QA support for the entire WSLH. The NADP Laboratory QA Manager attends EHD QA meetings, serves as the Non-Clinical Co-Chair of the QAC, and one CAL/HAL chemist is also a member of the QAC. Several NADP employees serve on subcommittees of the QAC and the WSLH safety committee.

2.3 WSLH Offices

The laboratory's analytical divisions are supported by the following: Office of Information Systems, Office of Finance (includes Purchasing, Accounts Receivable, & Accounting departments), Office of Human Resources, and Office of the Director (administrative support). WSLH support staff offices (e.g., Human Resources) work together with on-campus UW-Madison affiliates to hire staff, approve contracts, make purchases (both supplies and capital) and/or resolve information system issues. The WSLH Office of Finance works with a wide-variety of contracts and fee-for-service arrangements for private customers and industry, and facilitates complex long-term arrangements with state and federal agencies, other universities and international customers.

2.4 Laboratory Facilities

The CAL and HAL facilities are located at two WSLH properties in Madison. One location, off the UW-campus, is 2601 Agriculture Drive (AG) and the other location at 465 Henry Mall (HM), which is located on the UW-Madison campus. See Table 2 for activities at each location.

Table 2. Location of CAL and HAL Operations as of 6/2020

	NETWORK			
Process/Procedure	**NTN**	**MDN**	**AMON**	**Litterfall (Provisional)**
Sample Receiving	HM	HM	HM	HM
Supply Receiving	HM	HM	HM	HM
Supply Cleaning/Assembly	HM	HM	AG	HM
Sample Filtration	HM			
Sample Digestion/Extraction/Grinding		AG	AG	AG
Analytical - except pH/Conductivity	AG	AG	AG	AG
Analytical-pH/Conductivity	HM			
Final Data Review	AG	AG	AG	AG
Quality Assurance	AG/HM	AG/HM	AG/HM	AG/HM
Archive Storage	HM		HM	AG

2.5 Building Security and Access

Access to the WSLH locations is restricted to authorized individuals to ensure the safety of all staff members and to maintain sample integrity. All authorized visitors to the labs must be signed in and out of the building, wear a visitor badge, and be escorted by a WSLH employee. See the Labwide SOPs including **GENOP 1101** and **1004** for the specifics of security and access O:\SOP\Labwide SOP Policies\Final.

2.6 NADP Lab Management

The NADP laboratories are led by a team of managers who report to the EHD Director, David Webb, who in-turn reports to the WSLH Director/NADP PI - Dr. James Schauer. The Systems QA Manager, Dr. Martin Shafer; CAL Lab Manager, Chris Worley; HAL Lab Manager, Mark Olson; Sample and Data Processing Manager, Amy Mager; and QA Manager, Camille Danielson; all work together to manage the day to day laboratory operations. The Systems QA Manager and the QA Manager work independently of the day to day operational management of the laboratories. QA policies and initiatives are established to meet the needs of the NADP and any significant changes to methods or policies are assessed by the full management team. In addition, the team works closely with the NADP PO as well as the NADP Quality Assurance Advisory Group (QAAG) to ensure that the best interests of NADP are met. Monthly meetings are held involving all management from the CAL, HAL and the PO. All managers also are members of the NADP QAAG. Refer to **Appendix A** for the Laboratory Organizational charts.

2.6.1 CAL/HAL Lab Managers

The lab managers oversee the analytical staff of their respective groups. The lab managers handle troubleshooting of instruments, ensure that there is always sufficient lab staff coverage, assist with chemical analyses when necessary and confirm that sample analyses are completed within holding times. Personnel training and performance management is the lab managers' responsibility for the inductively coupled plasma optical emission spectroscopy (ICP-OES), flow injection analysis (FIA) and ion chromatography (IC) and cold vapor atomic fluorescence spectroscopy (CVAFS) analysts. The lab managers review and/or create analytical lab documents, SOPs, and reports. These managers are also responsible for reviewing the monthly budget statements to ensure the lab meets overall program budget goals.

2.6.2 Sample and Data Processing Manager

The Sample and Data Processing Manager provides oversight of the shipping and receiving staff, sample preparation and pH/conductivity chemists, and the assistant data managers. This manager ensures that adequate supplies are on hand and that supplies are properly prepared and sent in a timely manner to the network sites and that samples are received and initially processed in an appropriate and efficient manner. Field data entry review, analytical data review and validation, reporting to sites and publishing data to the PO are also overseen by the Data Processing Manager.

2.6.3 QA Manager

The QA Manager is responsible for implementing and maintaining quality assurance procedures throughout the NADP laboratories (both CAL and HAL). The QA Manager works with the other managers to verify that QA procedures are followed by all staff. The QA Manager is responsible for monitoring analytical and supply QC data for trends, management of documents, serving as the NADP QAAG Co-chair, conducting annual internal audits, managing analytical performance

evaluation (proficiency testing) samples, coordinating the preparation/review of SOPs and QA documents (including the QAP), and calculation/evaluation of QC limits/MDLs. The QA Manager is also engaged in WSLH division-wide and labwide initiatives and duties as a member of the EHD QA Team, as the Co-chair of the WSLH QAC and is a member of the Occurrence Management, QA Training, QA Metrics and Document Control subcommittees. This level of involvement ensures that the NADP QA practices are developed with external input and also meet labwide QA requirements.

2.6.4 Systems QA and Special Projects Manager

The Systems QA Manager is responsible for higher level QA of the entire NADP program. This includes oversight over the CAL and HAL, oversight of field QA, and making scientific judgements regarding recommended changes to NADP laboratory and field operations. This manager designs and implements QA tools to assess the robustness of the NADP systems and assists other NADP managers in trouble-shooting methods. The Systems QA Manager reviews all requests for special studies and evaluates the potential use of NADP samples by outside researchers, for scientific merit. The Systems QA Manager serves as the Co-chair of the QAAG and reviews all systems QA documents and provides technical support to the laboratories.

2.6.5 Laboratory Staff

It is the responsibility of the frontline laboratory staff (bench chemists and all support/administrative staff) to produce high quality data within the individual methods and within the parameters of the laboratory's QC guidelines. It is also the responsibility of the staff to identify existing problems or inefficiencies, and to improve lab practices whenever possible. CAL and/or HAL management are to be informed by the chemists of any staff needs or concerns.

2.7 Overall Responsibilities of the HAL/CAL

2.7.1 Quality Assurance

- Laboratory Operations Quality Control
- Supply Quality Control
- NADP QAAG participation
- Annual Management System review
- Annual Quality Assurance Report
- QA Document Management
- Internal and External Audits
- Sample Archive Maintenance
- New Method Quality Assessment

2.7.2 Site Support Services

- Site Supply Shipments
- Sample Receipt
- Supply Preparation
- Site Communications
- Field Operations Support

2.7.3 Data Management

- NTN Database
- AMoN Database
- MDN Database
- Laboratory Information Management System (LIMS)
- Data Entry
- Data Validation
- Data Delivery to Sites and PO
- Participation on DMAG

2.7.4 Special Services

- Special Studies
- Research Projects

2.7.5 Analytical Services

- Sample Assessment upon Receipt
- Sample Preparation (Filtration, etc.)
- Chemical Analysis
- Primary Data Review/Peer Review
- Method Development

2.7.6 Support Services Supplied by WSLH (Not direct NADP Staff)

- Purchasing
- Billing/Accounts-Receivable
- Information Systems
- Human Resources
- Communication/Outreach
- Building Maintenance and security
- Safety
- Quality Assurance
- Shipping and Receiving
- Lab-wide policies
- Administration

2.8 Hiring Process

The WSLH, as part of the UW-Madison, must conform to the UW's hiring policies. These requirements are designed to ensure that the laboratory's hiring practices are fair and equitable and meet all Federal and State regulations. Ultimately they facilitate the hiring of highly qualified personnel. The WSLH Office of Human Resources (OHR) is responsible for developing and maintaining all policies, procedures, and documentation related to hiring WSLH personnel. All records associated with hiring WSLH staff will be retained by OHR. The OHR is responsible for the

maintenance and final disposal of these records. For hiring process information please refer to the HR Website http://slhicmsprod/administrative-services/human-resources/. Specific position descriptions for all personnel are located in the main WSLH HR Office at 465 Henry Mall.

2.9 Training New Employees

2.9.1 General Initial Training

Training of employees takes place in a logical progression that meets applicable legal and scientific requirements. The Office of Human Resources has a checklist for new employees (http://slhicmsprod/administrative-services/human-resources/) which includes lab-wide training requirements. NADP also has a new employee training checklist (see **Appendix B**) which ensures new employees receive all necessary training in both division-wide policies and NADP-specific policies and procedures. An experienced NADP employee and/or manager guides the new employees through the checklists. Employees are also required to review safety checklists with a safety officer or manager prior to working in the lab. Employees are required to review and sign off on the Chemical Hygiene Plan and Emergency Action plans for their work location within one week of hiring. If they work at both AG and HM they need to review the plans for both locations.

2.9.2 Data Integrity Procedures

The integrity of NADP data is of utmost importance. To help ensure that, all employees must sign off on and follow the "Data Integrity, Ethics, Data Documentation Procedure" for the WSLH, Environmental Health Division (EHD GENOP 029). This document includes the organizational ethics policy, WSLH policies relating to data integrity, steps for data integrity training documentation, methods for monitoring data integrity, and steps for reporting data integrity concerns.

2.9.3 Analytical Method Training

Analytical method training is for new employees who have completed the initial general training and for any employee learning a new laboratory procedure. The trainee will review the applicable SOPs as well as the instrument manual(s). He/she will observe an experienced analyst prepare samples and operate the instrument. He/she will then work under the direct supervision of the experienced analyst until familiar with the analytical procedures and successfully completing a demonstration of capability. Training includes sample handling and preparation, safety specific to the method, documentation procedures, calibration procedures, QC requirements, data management, data reporting, and troubleshooting.

2.9.4 Initial Demonstration of Capability

The trainee will perform an "Initial Demonstration of Capability" (DOC) after adequate training on the analytical method and document the results on the DOC Certification Statement. The DOC includes: independently setting up the instrument, including preparation of standards, completing a full calibration, establishing the "within run" QC, preparing samples and all other procedures involved with a normal sample preparation and analysis. The analyst will then analyze a set of unknown samples (between 12-15 samples) prepared by the QA Manager. Quality control standards, previously analyzed natural samples, previously analyzed proficiency testing samples (if available), and relevant standard reference materials are used to assess capability.

When initial DOC criteria have been satisfied and the experienced analyst, QA Manager and Lab (or Data) Manager are confident that the employee is thoroughly familiar with the test, that employee is

allowed to work on his/her own on that method with only routine supervision. In addition to the analytical DOCs (for CVAFS, ICP-OES, IC, NTN FIA, AMoN FIA, pH, and conductivity) there is an AMoN initial DOC required for the preparation and extraction of AMoN samplers. There is also an initial (no annual requirement) DOC required for syringe filtration processing at sample receiving. All CAL DOC procedures are described in greater detail on the applicable forms at: O:\Teams\NADP\NADP Lab\LAB Final Forms\DOCs.

2.9.5 Ongoing DOC

All employees receive ongoing training/assessment and must demonstrate continued proficiency on each platform. Whenever there is a major change in instrument type, personnel, or test method, then a new DOC must be performed. Annually, each analyst must demonstrate continued proficiency on technical methods for which they are responsible. This is accomplished by completing an "Ongoing DOC" which entails analysis of 4 unknown blind standards prepared by the QA Manager. The samples are analyzed within normal analytical batches/runs (including full calibration and all normal QC requirements). Status of DOCs is tracked here: O:\Teams\NADP\NADP Lab\DOC\DOC Tracking New 2020.xlsx.

2.9.6 SOP Updates

Analysts are responsible for notifying the QA Manager of needed updates to SOPs and must assist with the revision process. There is a tracking spreadsheet to track needed revisions for SOPs and the QAP as those changes are identified and implemented. This is located at: O:\Teams\NADP\NADP Lab\SOPs\NADP FINAL SOPs\NADP SOP Revisions needed.xlsx. When a new revision of an SOP is finalized, the revision tracking table in the SOP documents all the major changes and analysts who are responsible for that method (or serve as backup on a method), and all analysts must document their review of the new or updated method on their annual SOP review sheet. The SOP is given a new revision number and the Table of Contents must be updated.

2.9.7 Annual Document Review

At a minimum, all NADP employees must review and document on the Annual Review form (stored in employee file) all of the following NADP, WSLH EHD, or WSLH Lab-wide documents:

- Safety Checklist
- Chemical Hygiene Plan
- Data Integrity, Ethics, and Data Documentation Procedure
- Emergency Action Plan
- HIPAA Refresher
- Disability/Accommodation Training
- NADP CAL and HAL Analytical SOPs (as applicable to their position)
- NADP CAL/HAL QAP

2.9.8 CAL Annual Rotation

If possible, the CAL analysts will rotate analytical platforms annually at the manager's discretion. This provides multiple backup analysts on all platforms, facilitates new perspectives applied to each technology and can improve the engagement and proficiency of each analyst. Prior to rotating, each analyst must be thoroughly trained and successfully complete an initial DOC for any platform that is new to them and ongoing DOCs for platforms they are already proficient on and need to maintain.

Ongoing DOCs must be completed within one year of a previous DOC in order to maintain their acceptability as an analyst for a specific instrument platform. If more than 13 months has elapsed since proficiency was demonstrated, an initial DOC must be completed for that platform.

2.9.9 Training Documentation

All training forms, checklists, sign-off sheets, certification statements, and DOC forms related to the above requirements will be signed and dated by the employee and given to the Lab or QA Manager (as applicable). The QA Manager will ensure that the DOC documentation is complete and meets the criteria. The Lab Manager(s) will be responsible for general training records. Most training documentation will be filed in the personnel training files maintained by each manager. DOC documentation is maintained by the QA Manager. See **Appendix B** for tables of Training Requirements.

2.9.10 Additional Education/Training

In addition to specific subject matter/protocol training offered by the WSLH NADP organization, the laboratory supports continuing education that may include attending conferences, seminars, vendor training, or formal higher education. All employees are encouraged to keep up with changes or advances in analytical methods and instrumentation. This is done by circulating literature and other pertinent information as it becomes available. Through the UW there is also the opportunity to attend training or utilize resources such as LinkedIn Learning to become more proficient with software programs or other tools. Employees are also encouraged to present or attend seminars, brown bags and to be involved with NADP conferences. They are encouraged to be involved with other committees and other sections of the WSLH. As time allows, they are encouraged to design and implement research projects, conduct method development, pursue other innovative ideas, and to present such activity at NADP conferences.

3 Safety

The EHD safety committee meets regularly and conducts safety inspections. The Safety Committee membership consists of a cross section of laboratory personnel and at least one NADP staff member serves on the committee.

3.1 Employee Handbook

The Human Resources section of the Employee Handbook on the intranet (http://slhicmsprod/administrative-services/employee-handbook/) contains important safety-related information including policies on eye protection, fire extinguisher training, footwear in laboratory areas, glove use, and protective clothing. Included in the handbook are links to UW-Madison employee health and safety information. The WSLH also has a detailed “Chemical Hygiene Plan and General Laboratory Safety Plan” (AG DR SAFETY GENOP 102), which contains comprehensive information on general laboratory safety procedures and operations, including chemical storage, waste disposal, safety showers, fume hoods, controlling exposure, employee safety training, housekeeping, emergency procedures, and more. To ensure the safety and well-being of all WSLH personnel, new employees must become familiar with basic safety precautions before working in the laboratory, all employees must annually review the Chemical Hygiene Plan.

3.2 Safety Checklist

A key tool in safety training is the Employee Safety Checklist (separate checklists are in place for both HM and AG locations) which comprehensively lists safety issues such as safety shower and fire extinguisher locations, evacuation procedures, policies on eating and drinking in the lab, use of potentially dangerous instruments and chemicals, safety apparel use, fume hood use, and much more. The EHD Employee Safety Checklist also lists external references for additional information on laboratory safety. Employees are required to review the Emergency Action Plans annually.

3.3 Safety Resources

- Safety Checklist
- Chemical Hygiene Plan (AG and/or HM)
- Emergency Action Plan (AG and/or HM)

(See **Appendix B** Training Table for links)

4 Purchasing

4.1 Supplies

The WSLH Purchasing Department procures goods and services necessary for operations performed by the WSLH except as noted below. Ordering through the Purchasing Department is performed by submission of an E-48 form through the WSLH Intranet. The Purchasing Department operates under authority of the UW Madison Purchasing Department and must adhere to University and State of Wisconsin policies. In addition to submitting an E-48 to Purchasing, the NADP management team is authorized to order department supplies directly from specified vendors. These orders are placed through the University of Wisconsin's Materials Distribution Services (MDS) whenever possible.

4.2 Evaluation of Supplies

It is the responsibility of the individual user of supplies, reagents, and consumable materials to verify that the supplies are appropriate to meet requirements specified in the QAP and analytical SOPs. The managers will assist in this endeavor by purchasing supplies and monitoring those that need to pass QC checks prior to use. Managers will track budgets to ensure that purchases will meet the NADP budget expectations. Bottles, test tubes, filters, buckets, bucket lids, bucket bags, lid bags, and sampling bags are tested on a regular basis to confirm QC limits for contamination are being met. Individual technical SOPs also state specific grades of reagents, standards, or chemicals required for the procedure and their storage requirements. Supply QC is covered further in Section 8.0.

4.3 Capital Equipment

Capital equipment purchases (i.e. > $5000) are subject to special procurement requirements. Unless the item(s)/vendor are under contract to the University; the purchase will need to be bid (if >25K) or 3 quotes obtained (if between 5K and 25K). The Lab Managers facilitate capital equipment requests. All capital equipment requests must be approved by NADP Managers, the Lab Director and Chief Finance Officer and procured through the WSLH Purchasing Department.

5 WSLH Information Systems

5.1 General Infrastructure

The WSLH Office of Information Systems (OIS) has in place numerous protocols to ensure the integrity, security, and reliability of the IT systems. These include:

- A dedicated secure data center that meets "best practice" standards including climate control, uninterruptable power supply (UPS) and generator backup power, multiphase fire suppression system, physical security safeguards and other safety features (e.g. emergency lighting).
- Separate test and production systems are put in place whenever possible so that changes in systems can be tested prior to being implemented in production. The changes are done following a "Change Management" process and documentation is kept in computer "footprints" system of all changes.
- Nightly backups to tape using a grandfather-father-son rotation scheme with weekly offsite rotation (both onsite and offsite tapes are stored in "media proof safes" which are UL-125 rated to not exceed 125°F). All shared drives are flash copied at set intervals during the day to preserve changes made since the last backup (allow for more recovery options).
- Multiple, redundant network paths for servers and workstations include 2 firewalls that establish a secure IPSEC tunnel between primary buildings. All network traffic between each location is connected through a fiber-optic ring owned by the "Metropolitan Unified Fiber Network (MUFN) Consortium" <https://mufn.org/> (of which WSLH is a voting member) back to the UW-Madison campus and protected behind firewalls. The UW-Madison is the Internet service provider for both laboratories. Secured virtual private network (VPN) service with Remote Desktop Connections (RDC) is used for remote access to enterprise resources. Numerous security controls are in place to prevent unauthorized access.
- Inventory and asset management tools/techniques including anti-malware/antivirus, periodic searches for sensitive or restricted data and routine patching for operating system and 3rd party patches (e.g. all servers are patched within 30 days of update release) are in-place.

5.2 Instrument Workstation Protection

- Rather than rely on operating system patches which can negatively impact instrument acquisition/analysis software functionality, instrument workstations are protected by 2 different segregated VLAN's (virtual networks) with firewalls to maintain a robust data acquisition capability:
- Instrument VLAN - contains instrument workstations where laboratories can run antivirus/anti-malware software. These PCs are allowed open access to internal servers but Internet traffic is restricted to only a small number of whitelisted sites (e.g. www.PerkinElmer.com).
- Protected VLAN – contains instrument workstations that cannot run antivirus/anti-malware software or those that meet other high-risk criteria. These PCs have very limited access to internal resources and no Internet access.
- When possible, instrument interfaces are established to directly pull data into the LIMS systems. Most NADP instruments do not have this capability but pH and conductivity do interface directly with NADP LIMS "Benchchem". Instrument data is stored locally and then backed-up to shared drives on the network using a centralized job scheduler (i.e. the instrument workstation is configured to store its data on the local C:\ drive and then at scheduled times is picked up and copied by one of the laboratory servers' Document Control Systems).

5.3 NADP LIMS

The CAL and the HAL utilize a custom-made LIMS system. The system is made up of multiple components that are utilized by personnel depending on their roles. These are the systems commonly used and their main functions:

- **Benchchem** – used to add QC samples, review QC results, print additional bottle labels, look up sample results, complete AMoN extractions and WI/WD preparation (balance interface)
- **Instrumental Chemistry** – used for upload of instrument results, also can do most of the same functions as Benchem
- **NADP Address Book** – used to record site information (status, address, contacts, equipment type)
- **NADP Data Entry** – used to assign a unique ID to each sample and to enter data from the field form. Also used to track supply requests and shipments.
- **NADP Data Review** – used to review sample field and lab data resulting in quality rating for each sample. Used to generate and send data reports to individual sites.
- **NADP Data Management** – Only used to send AMoN reports, but soon will be able to do through the Data Review program.

6 Records

6.1 QA Document Maintenance

All documents related to laboratory processes are required to have appropriate document control (unique title, revision number, effective date and page numbers at a minimum). This includes SOPs, forms, benchsheets, plans, and reports. Laboratory staff are required to read the CAL/HAL QAP and relevant SOPs annually. The QAP and analytical SOPs will be reviewed for updates and corrections annually. Non-analytical SOPs will be reviewed for corrections at least every 3 years. All revisions will be numbered and dated; previous versions will be kept in the electronic archive files for reference. The QAP and all SOPs will include a revision table in which any substantial changes to the content will be detailed for each version for future reference. A searchable Table of Contents listing all SOPs and their current status is provided in the Final SOPs folder as well as on the NADP website. A copy of any SOPs can be obtained at any time upon request. The list of SOPs can be found at the "laboratory SOPs" link found on this page: http://nadp.slh.wisc.edu/NTN/NTNLAb.aspx.

6.2 Standard Operating Procedures

SOPs are written and maintained for all NADP functions. In addition, there are SOPs that apply to operations covered by this QAP that play-out at three different levels within WSLH:

- Lab-wide SOPs: O:\SOP\Labwide SOP Policies\Final
- Division-wide SOPs: O:\SOP\EHD\Division Wide\Final
- NADP Department-specific SOPs: O:\Teams\NADP\NADP Lab\SOPs\NADP FINAL SOPs

6.3 Laboratory Notebooks

A laboratory notebook is any physical book in which testing data is recorded; this includes experimental data, standards logs, instrument logs, etc. All laboratory notebooks are assigned a unique number by the QA Manager and tracked: O:\Teams\NADP\NADP Lab\QA\Lab Notebooks. The labs are moving towards electronic versions of lab notebooks wherever possible to provide easier access at

all locations and more efficient processes. The chemical and reagent tracking notebooks are now stored online: O:\Teams\NADP\NADP Lab\NADP ELN for stocks and Prepared solutions (see Section 8.7).

6.4 Instrument Records

The QA Manager maintains a list of the instruments and support equipment, including make and model, type of analysis conducted, and physical location in the lab. See **Appendix C** for a list of major analytical equipment. The list also records the instrument serial numbers and an assigned unique NADP instrument number. The NADP Equipment Log is located at: (O:\Teams\NADP\NADP Lab\Equipment\NADP Equipment Log.xlsx). Instrument maintenance and verification procedures are documented in the appropriate SOPs, and maintenance issues are recorded in the applicable instrument laboratory notebooks.

6.5 Records Disposition Authorization

Records Disposition Authorizations (RDAs) are also called records schedules. RDAs are key instruments for establishing a records management program for organizations within Wisconsin State government. In essence, records schedules describe the organization's information resources, how long they are going to be retained, and what their ultimate disposition will be. They are the policy statements that govern the ultimate disposition of records. Some EHD records fall under General Records Retention Schedules (GRS), which are approved for UW-Madison use. General records schedules codify retention policies for record types that are common to all offices across the UW system. Refer to https://www.library.wisc.edu/archives/records-management/retention-disposition/general-records-schedules/. The EHD also has a unique records schedule, which covers records not included in any campus-wide GRS. It can be found at: O:\RDA's\Final RDA\EHD_2017_WSLH.pdf. NADP will follow the EHD RDA which requires a minimum of 6-year retention of all associated records after analytical testing is complete unless otherwise instructed by the NADP Executive Committee.

6.6 Storage of Paper Records

Refer to ***Labwide GENOP 1002***, "Records Storage and Disposal," for storing documents in record storage boxes. Boxes may be immediately sent to the State Records Center https://doa.wi.gov/Pages/StateEmployees/StateRecordsCenter.aspx or may be placed in an approved storage area at the WSLH for up to 3 years (after which they will be sent for storage). Approved storage areas are specific locations where new inventory may be added. The approved storage area for AG is Room 14. Records are stored in Room 121 at Henry Mall. Complete documentation of items placed in storage must be maintained by the QA Manager with assistance from a designated records coordinator. The records coordinator has the responsibility of knowing what is in each box, where each box is located, and the destruction date of each box. NADP records storage is recorded here: O:\Teams\NADP\NADP Lab\Records Management\NADP Archived Paper Records.xlsx. Labwide GENOP 1002 also details the procedure for immediate destruction of records and the procedure for storage of electronic records.

7 Instrumentation and Equipment

The NADP CAL and HAL rely on complex analytical instrumentation. It is imperative that all equipment and instruments are calibrated, verified, operated, and maintained in a proper manner to obtain reliable data. Instruments dedicated to the NADP were purchased to provide the needed

analytical capacity and due to the unique nature of NADP samples.

7.1 Instrument Failure/Maintenance

If an instrument fails to operate within defined limits or specifications, then corrective action is performed, and samples are reanalyzed or qualified as required by the method. It is the responsibility of the analyst to notify the CAL or HAL Manager if non-routine maintenance is required. Instrument vendors will be contacted if troubleshooting is unsuccessful. Preventive maintenance (general maintenance) should be performed at the frequency recommended by the manufacturer to avoid instrument failure. Preventive maintenance and corrective action is always recorded in the instrument logbook. WSLH has back up capability utilizing identical or similar instruments for all platforms in other WSLH departments that could be used if necessary.

7.2 Laboratory Reagent Grade Water

7.2.1 Reverse Osmosis (RO) water

RO water is plumbed to all the laboratories at the AG facility and the RO systems are maintained by a service contract with a water treatment vendor. The final treated water is American Society for Testing and Materials (ASTM) Type II and is used to feed the ultra-pure polisher systems and to operate the NADP dishwasher in room 200B. DOA controls the AG RO systems. At HM, an RO system (with post mixed-bed resin treatment) was installed by NADP which directly feeds a polisher system and the NADP dishwashers used for bucket and bottle washing. The electrical resistance of the RO water at HM, and other pressure gauges, is recorded each work day on the hard copy log in the tank room. The log form can be found at: O:\Teams\NADP\NADP Lab\LAB Final Forms\Water System and Temperature logs\RO System Log.xls. The HM resistance meter should read > 18 MΩ-cm when in use. If there are issues with RO systems DOA or the service vendor will be contacted and an occurrence will be recorded.

7.2.2 Type I Water

Elga Purelab Ultra Milli-Q polishers are located throughout the laboratories and provide point-of-use ASTM Type I water to NADP labs. NADP purchased 4 Type I water systems - two located at HM and 2 at AG. Type I water is referred to in NADP documents as Type I or Milli-Q (MQ) water. There are also other Milli-Q systems throughout AG that may be used to obtain Type I water. The non-NADP systems are monitored/maintained by their respective departments and serviced on a regular basis. Lab analysts will not use any Type I water if the resistivity reading is less than 18.2 MΩ-cm. Type I water is used in the preparation of glass/plastic-ware, reagents, standards, and QC samples (analytical blanks, method blanks, supply QC). There is a service contract with a water treatment vendor to maintain the polishers. On a six month schedule the vendor will exchange the carbon filter, the mixed bed cartridges and the organic scavenging Type II ultra-pure anion resin. The UV filter will be changed based on the number of hours of use. Please see EHD GENOP 032 “Monitoring and Maintaining Water Purification Systems”, for specific water purification system monitoring and maintenance procedures. NADP staff record the resistivity readings each day of use for each system and MQ system blanks are taken weekly by NADP and are tested for all applicable analytes. If the resistivity is below 18.2 MΩ-cm corrective action is taken and a manager is notified. If the resistivity reading or analytical data does not meet criteria an alternate Type I system that meets criteria is used until the issue is resolved.

7.3 Refrigerators, Freezers, and Temperature Monitoring

NADP maintains daily temperature and min/max records of its temperature sensitive equipment. Thermometers are verified at least annually against a certified National Institute of Standards and Technology (NIST) thermometer and correction factors applied if necessary or a new thermometer is purchased. Refrigerator thermometers must be within 1.4° C of the certified or need correction factor or replacement. Freezer thermometer must be within 5°C of certified or use correction factor or replace. Temperatures are measured every business day in all sample storage units and min/max thermometers show overnight/weekend variances. The min/max is recorded and reset each business day so that min/max temperatures are monitored until the next business day. Refrigerators are expected to be in the range of 2 to 6 °C and freezers should be from 0 to -40 °C. An occasional 1-2 degree variance on the refrigerators is acceptable if the staff know that the doors have been open for sample reorganizing. Otherwise, the out of control temperature should be verified with a 2nd thermometer and corrective action including possible adjustment of the thermostat, replacement of thermometer batteries, and calling for service if the issue cannot be corrected.

7.4 Analytical Balances

Analytical and top-loading balances are monitored for proper operation and accuracy by using NIST Traceable Class 1 weights each day before use (some balances used are maintained by the EHD Inorganic Department) and data recorded in a logbook or on a spreadsheet. Analytical balances will be serviced when test weight values are not within the manufacturer's instrument specifications. NADP reference weights are submitted for external verification or replaced every 5 years. The analytical balances are certified annually by an outside company and records can be found at: O:\Teams\QAC\QC Documentation\Balances\. The AMoN (extraction) and MDN (login) balances are directly interfaced with the CAL and HAL LIMS to import weights directly into the programs.

7.5 Pipettes

Pipettes are verified quarterly with 4 replicates each of 3 different volumes over the range of use. Annual verification and preventative maintenance on the pipettes is performed by an outside vendor who documents performance as submitted and performance as returned. Internal verification is primarily done by the gravimetric method although very low volume pipettes are normally tested using the colorimetric instrument. When pipettes fail the criteria they are retested, if repeated failure occurs corrective action is taken. The pipette may be adjusted and retested or sent to a certified verification expert for recalibration/repair. Verification records are kept at: O:\Teams\NADP\NADP Lab\QA\Pipette Verification and in hard copy files which the QA Manager maintains.

7.6 Traceability of Measurements

7.6.1 Standards and Reagents

Standards and reagents of required purity are obtained from approved suppliers. It is preferred that standards be certified and be traceable to the NIST. Analysts need to be aware of expiration dates and notify a manager when those dates are approaching. The staff person checking in or preparing a chemical labels the bottle using either the prepared standards label or the stock label which includes expiration dates as well as the NADP code. The templates for these stickers is found here: O:\Teams\NADP\NADP Lab\QA\Labels\Chemical label Templates.

7.6.2 CAL Standard and Reagent Tracking

Chemicals, standards and reagents that are purchased (referred to as "stocks") are recorded in the electronic lab notebook: O:\Teams\NADP\NADP Lab\NADP ELN for stocks and Prepared solutions\2020 Stocks Chemical Tracking.xls. The "stock" code is written as "NADP", followed by a dash, the year received, a dash and then "S" for stock and the next sequential spreadsheet number. Stock example: NADP-20-S12 for the 12th stock logged in 2020.

A second spreadsheet is maintained for prepared chemicals – these are dilutions or mixes of stocks and/or reagents that have been prepared in the lab: O:\Teams\NADP\NADP Lab\NADP ELN for stocks and Prepared solutions\2020 Prepared Chemical Tracking.xls. The "prepared" code is written as 'NADP" followed by a dash, the year prepared, a dash, and then "P" for prepared and the next sequential number within the spreadsheet. Prepared solution example: NADP-20-P35 for the 35th prepared chemical mix in 2020.

Each quarter a PDF copy of the electronic notebooks including the audit trail (tracking of the changes) will be saved. Where applicable (required for certified standards), the certificate of analysis is labelled with the unique ID code from the notebook, scanned and filed in to the electronic COA file (O:\Teams\NADP\NADP Lab\Certificates of Analysis). A hard copy does not have to be kept if there is a scanned copy. Material Safety data sheets are also scanned and saved for each type of chemical used at the lab: O:\Teams\NADP\NADP Lab\Safety\MSDS.

7.6.3 HAL Standard and Reagent Tracking

The HAL has their own chemical and reagent tracking documentation. Stock materials purchased from a manufacturer are logged into physical notebooks (tracked by EHD Inorganic QA). Mixed reagents and working standards for mercury analysis are tracked electronically and are located here: M:\EHD\ESS(4900)\ESS Inorg(4910)\METALS\Clean Room\1Mercury\Hg Standard LogBook #93. The HAL stores COAs as hard copies, bound and maintained in a laboratory cabinet. All standard and reagent bottles are dated when received and expiration dates are recorded to monitor the shelf life. If an expiration date is not provided by the manufacturer no expiration date documentation is required, however the method should be checked for expected shelf life of the substance. All chemicals will be replaced prior to their expiration date.

7.6.4 Traceability

All analytical results and measurements are traceable to standards, reagents, reference materials, and instrumentation. Working standards and reagents are tracked for each analytical run using a cover sheet which has the documented traceable unique codes. Analytical instrumentation and equipment (including pipettes) are assigned identification numbers, which are also tracked to each analytical runs. Date and time of analysis and analyst initials are documented per analytical run. For NTN and AMoN analysis a "Peer Review Cover Sheet" (O:\Teams\NADP\NADP Lab\LAB Final Forms\Peer review) for that particular platform is completed each analysis day which records all of this information. The HAL uses these peer review sheets: M:\EHD\ESS(4900)\ESS Inorg(4910)\METALS\Clean Room\1Mercury\Total Mercury\Bench Records\Total Mercury in Water TEKRAN Template Rev 1.doc and M:\EHD\ESS(4900)\ESS Inorg(4910)\METALS\Clean Room\1Mercury\Methyl Mercury\Bench Records\MeHg in Water TEKRAN Bench Record.doc. Data from the instruments is saved in electronic files on the WSLH shared drives. All results are directly linked to each sample via the unique sample ID number.

8 Supply QC

Each network under the NADP long-term monitoring program requires very specific sampling supplies and robust protocols for their preparation to maintain data consistency throughout the networks. The quality of the supplies provided by the CAL and HAL must be consistent across and within sites. The laboratories must provide clean and validated supplies for NTN, MDN, AMoN and the Litterfall initiative.

8.1 Supply Blanks

8.1.1 A variety of CAL and HAL site supplies are routinely checked for contamination. These supplies include, but are not limited to:

- Type I water
- Test tubes (for instrument autosamplers)
- NTN collection buckets and lids
- NTN (1L) HDPE sampling bottles
- NTN 60 mL HDPE sample bottles
- NTN polyethersulfone filters
- NTB Bucket and lid storage bags
- NTN sampling bags
- AMoN Radiello cartridges, Radiello cores and glass shipping jars
- MDN acid baths
- MDN preservative HCl acid
- MDN PETG 250 mL, 1L and 2L bottles
- MDN sample trains – funnels and thistle tubes

8.2 New NTN and MDN Supply Assessment

New NTN and MDN supplies that are not routinely pre-washed must meet "Lot QC" requirements per ***NADP SOP 200*** "New Bottle and Test Tube QC Check". New lots of bottles, test tubes, filters, and sampling bags must meet established lot-based criteria before use within the networks. MDN supplies are covered in ***NADP SOP 405*** MDN Supply Preparation.

8.2.1 CAL New Filter Lot Testing

Polyethersulfone 0.45 µm filters (disc and syringe) are used to remove the particulate matter from the bulk NTN precipitation samples; leaving an operationally defined soluble/dissolved fraction for chemical analysis. The filter-collected particulate matter is normally discarded. Extractable contaminants (all the NTN analytes) in these filters are assessed in each new filter lot prior to use. Ten filters, pulled from at least three different boxes (boxes of 100 filters) of the same lot number, are tested. New syringe filter lots are tested at a minimum rate of 5 per lot of 150 or less and 10 for lot sizes of greater than 150.

Disc filter blanks (on-going) are also performed on each day that field samples are filtered, one at the beginning and one at the end of the day. On-going syringe filter blanks are performed weekly.

8.2.2 CAL New Bottle, Bag and Test Tube Testing

All new bottle and bag lots are tested without rinsing by filling them with the designated volume of water and letting them sit at least overnight at room temperature before analysis for the NTN analytes. Test tubes are filled with Type I water, and tested the same day. Ion Chromatography (IC) autosampler tubes are cleaned before use and not subject to this lot testing process. The IC method blanks will also serve as an assessment of potential contamination. The pH/conductivity tubes are not tested, but conductivity blanks are run every 10 samples in the same tubes and to indicate possible contamination.

8.2.3 CAL Lot Testing Criteria

The lot testing criteria states, for each NTN analyte, that the mean of at least 10 samples per lot must be < NTN MDL_N and none of the supply blanks in the batch tested may exceed 3 times the NTN MDL_N. See **Appendix D** for MDL Tables. If the criteria are met, then the new lot can be used. If the QC criteria are not met, then another set of 10 may be tested, or the entire lot may be rejected and returned to the manufacturer. If the second test fails, the lot must be rejected. For batches of filter or bag supplies greater than 1000, a minimum sample set of 20 QC checks are analyzed.

8.2.4 HAL New Bottle Testing

PETG bottles are purchased in large lots and must be tested prior to being accepted for use within the MDN. For a new lot of over 200 bottles, 10 bottles must be tested for total mercury content. For lots of fewer than 200, 5 bottles will be tested. To test, each bottle is pre-charged with the standard quantity of preservative acid, and then 100 mL of Type I water is added. Each bottle is then capped, labeled and bagged for analysis at least 12 hours later.

8.2.5 HAL 1% HCl Preservative acid

Each new batch of sample preservative acid must be tested for total mercury content to verify cleanliness prior to use.

8.3 Ongoing NTN and MDN Supply Assessment

Data from the ongoing supply QC program is assessed on a quarterly basis at a minimum. Refer to **Appendix E** for details of all ongoing supply QC frequencies and criteria. Analysts are also asked to notify the QA Manager if they notice high supply blanks in analytical runs. QC samples are identifiable in a general way by their Sample ID which always begins with the year. There may be unknown PT samples mixed with QC but the analysts know to alert the QA manager to any significant detections of analytes. NADP reused (or new and washed) supplies are assessed for values above the supply rejection criteria which is set to the NTN MDL_N for NTN and MDN criteria as outlined in ***NADP SOP 405 MDN Supply Preparation***.

8.3.1 HAL 30% HCl Acid bath testing

The acid baths that are used to clean funnels and thistle tubes are tested for total mercury monthly. The HAL is determining what the criteria should be to indicate the acid baths must be drained and refilled. That level will be determined by the bath concentration that is correlated with high sample train blanks.

8.3.2 HAL Sample Train testing

Weekly, a funnel and thistle tube are randomly selected for QA testing. The glassware is dried, bagged, and stored a minimum of 2 days prior to testing. To test, the analyst assembles the sample train and flushes 100 mL of Type I water through it and into a clean 1L PETG bottle. It is capped, labelled, bagged, and sent to AG for processing and analysis.

8.4 AMoN Supply QC

Only Passive Diffusion Samplers (PDS) approved by the NADP are used for sampling (currently restricted to Radiello® products). As outlined in **Appendix E**, "AMoN Supply QC", the diffusive bodies (both new and used) and cores are tested as well as the glass storage/shipment jars and the water used for core extraction. Also monitored is the background level of ammonia in the room and hoods in which the AMoN samples are processed. Refer to ***NADP SOP 400 AMoN Preparation*** and ***NADP SOP 502 Determination of Passive Ammonia by FIA*** (measuring ammonium) for more details of AMoN supply preparation and analysis.

8.5 Supply QC Log In

Supply QC samples are logged into the "Benchchem" application of the NADP LIMS. The samples are added under the appropriate "Projects" using the Supply QC Log In and Frequency Table (O:\Teams\NADP\NADP Lab\LAB Final Forms\Supply QC Protocol\Supply QC Log In and Frequency.xlsx, see **Appendix E**), to fill in the "Client" and "Description" fields. A bottle or tube label will automatically print out and must be affixed to the corresponding bottle or tube.

9 Sample Processing and Chain of Custody

9.1 Sample Processing Overview

Detailed information on sample processing for the NADP NTN, MDN, and AMoN networks is contained in the applicable SOPs. For sample log-in specifics refer to ***NADP SOP 100 Sample Log In and Data Entry*** for all three networks.

Samples are logged in by entering information from the field forms into the NADP Laboratory Information Management System (LIMS); and from there data flows to the network database.

Each incoming sample is identified by a unique laboratory number (LABNO) and station identification code (Site ID). These designators remain linked to the sample throughout sample analysis, data verification and final data transfer to the PO. For the NTN a single analytical bottle is prepared from the filtered sample on receipt and shared between platforms. MDN samples are collected directly into the acid-charged sample bottle, which after receipt at HM is shuttled to AG for digestion and analysis. AMoN samplers are shipped in glass jars inside of boxes.

Table 3. Network Sampling Information

Network	Preserv.	Prep	Field Deployment Time Flagged	Field Hold Time Flagged Receipt >	Lab Hold Time Flagged Analysis >
NTN	4-6°C	Filtration	>194 hours = QRC	>16 days after off date = QRB >60 days after off date = QRC	>60 days from receipt = QRB (Internal tracking/goal of 21 day HT)
AMoN	Frozen	Extraction	>360 hours = QRB	None	>21 days from off date = QRB
MDN	1% HCl	Oxidation/ Distillation	>194 hours = QRB	>16 days after off date = QRB >30 days after off date = QRC	>60 days from receipt = QRB

9.2 Chain of Custody (COC)

Samples arrive at the CAL/HAL with a field form which contains all the sample and site information for that deployment. A unique barcode identification number is obtained from the LIMS and is placed on the sample bottle (sample bag for AMoN) at log in on the business day it is received. For NTN, the same unique ID is applied to both the 1-liter sample bottle, and the associated 60 mL analytical and 60 mL archive bottles. AMoN sample bags (with glass jar inside) receive an "N" number which groups the samplers from a site together if there are duplicates or travel blanks. Then each sample gets a unique sample ID number which is placed on the bag, and then a label sticker matching that ID is printed and placed on the extraction tube(s) when each sampler is extracted. The barcode labels are traceable to the field forms and the LIMS. Chain of custody is maintained electronically in LIMS, with a record of receipt date, analysis date and link to the scanned field forms. Samples must be shuttled from HM to AG, and documentation of this process is kept here: O:\Teams\NADP\NADP Lab\AG Drive Sample Check In. Refer to ***NADP SOP 100*** for sample log-in and COC processes.

9.3 Analytical Sample Storage

For the NTN samples, high density polyethylene (HDPE) bottles of 60 mL or 1 L volume are used for sample storage (at 4°C). AMoN sample extracts are stored in Radiello® tubes (frozen) while AMoN QC samples (that don't include a core extraction) are stored frozen in Lachat test tubes after extraction or preparation.

Analytical NTN and MDN samples are discarded after the sample data are published to the PO. AMoN samples are kept frozen in the original extraction or analysis tubes. The acidified and brominated MDN samples are stored in their one or 2 L PETG collection bottles until the data are published.

9.4 NTN Sample Receiving and Processing

NTN samples received at HM are logged into the LIMS, assessed for leaks, approximate sample volume and contamination. Samples are analyzed for pH and conductivity and then filtered on the day of receipt (assuming receipt Monday – Friday) if possible. Field form data is entered on receipt into

LIMS and then a second data entry is done by another person. Samples received over the weekend/holidays are processed on the next business day. In the winter, samples received frozen are normally processed the next business day due to the need for thawing. The 1 liter NTN sample bottles are tracked in LIMS using a barcode system that determines the number of uses. After 10 uses, the sample bottle is marked at log in and recycled after sample processing is completed.

9.4.1 NTN Sample Processing

All NTN samples that are analyzed are filtered (as of January 2020 WI/WD change). If possible, two 60 mL bottles of filtrate are collected; the first for the analytical sample and the second for an archive sample (if sample volume is sufficient). This archive bottle is marked with a yellow sticker and stored frozen. Samples must be analyzed for all NTN parameters unless there is insufficient volume to do so, in which case the sample is designated as a wet, incomplete (WI) sample. All samples less than 28 mL are syringe filtered (as opposed to 47 mm disc filter) due to the small volume of sample. Samples between 4 and 13mL (Wet Incomplete = WI) original volume will be syringe filtered and diluted to 15 mL so that they can be analyzed for all parameters except pH and conductivity. Samples between 14 and 27 mL will have 8 mL poured off for pH/conductivity and the remaining 6 - 19 mL is syringe filtered and diluted to 15 mL total (Wet Dilute =WD). If the sample volume is ≥ 15 mL after filtering it will not be diluted. Samples with <4 mL (Trace) are not analyzed. The dilution of WI and WD samples allows analysis by FIA, ICP and IC for all NTN analytes. See **Appendix F** for a schematic diagram of the NTN sample analysis process based on sample volume.

9.4.2 NTN Sample Preservation:

Samples are refrigerated upon receipt. After initial sample processing (below) the filtrates are refrigerated, and the excess sample volume is discarded (unless requested for a special study).Archive samples are frozen as soon as possible after preparation. Refer to Table 3 above for network sample details.

9.4.3 NTN Volume Assessment

Lab Codes (for sample volume):

- W (“Wet”) = ≥ 28 mL
- WD (“Wet Dilute”) = 14-27 mL
- WI (“Wet Incomplete”) = 4-13 mL
- T (“Trace”) = < 4 mL
- D (“Dry”) = 0 mL

9.4.4 NTN Sample Collection Deployment Period

Bucket samplers should be deployed for 7 days (168 hours), but other deployment periods may occur due to operators’ schedules, holidays, and national emergencies/shutdowns. A sampling period for > 194 is coded as invalid (QR=C).

9.4.5 NTN Hold Time

All NTN sample analyses, except for pH and conductivity, are to be completed within three weeks of sample receipt at the CAL. If the lab exceeds 3 weeks a qualifier note is added to the possible qualifiers spreadsheet. If lab analysis occurs over 60 days from receipt, then a T6 error code will be

recorded in the database. The pH and conductivity analyses are to be completed within 3 business days of sample receipt. Sample receipt is defined as the date sample is logged into the NADP LIMS system. Sample receipt date = login date. The login date is normally the same as the actual physical sample receipt date but may be 1-3 days later if the sample is received near the end of the day or on a weekend/holiday.

9.5 AMoN Sample Receiving and Processing

AMoN passive samplers are logged into the LIMS each business day that they are received at HM, sent to AG via courier, and placed into the freezer. Broken glass jars or other issues are noted in the LIMS comment section at sample receiving when possible.

9.5.1 AMoN Sample Processing

The AMoN passive samplers are extracted in batches on designated extraction days in low ambient ammonia lab under an ammonia scrubbing hood. Normal extraction batches range from 40-80 deployed samples plus QC samples. The AMoN extraction process is outlined in ***NADP SOP 401***. At extraction, they are assessed for major field/shipping issues such as broken or dirty bodies, and notes are recorded in the LIMS and are linked to the sampler ID for possible flagging. See ***Appendix G*** for sample notes and QR code information. After an overnight extraction in high-purity water, samples are analyzed for ammonium by FIA (see ***NADP SOP 502***).

9.5.2 AMoN Sampler Deployment/Storage

Prepared passive samplers (refer to ***NADP SOP 401*** for AMoN sampler preparation) are placed into glass jars and then stored in a freezer until they are shipped out to the field sites. Samplers are deployed for 2 weeks. Samplers are placed back into the glass jars and Ziploc bags and sent back to the CAL in the dedicated shipping box.

9.5.3 AMoN Sample Hold Time

AMoN sample extraction and ammonium analysis must be completed within 21 days of “date off” (date when collected in the field) otherwise a data qualifier “y” flag (resulting in quality rating QR=B) is assigned for delayed sample processing. If samples cannot be analyzed within 21 days of date off, a qualifier will be added to the sample qualifier spreadsheet O:\Teams\NADP\NADP Lab\Possible data qualifiers\NADP Sample Qualifier INFO.xls. Refer to Table 3 above for network sample details.

9.5.4 Radiello® Body Usage

Each Radiello® body is cleaned (see ***NADP SOP 400***) and used for 5 deployments before being taken out of circulation per manufacturer’s recommendation. After 5 deployments, the permeability of the body may be affected. The CAL plans to study this in the future and may change this practice if it can be shown that they can be successfully used for more deployments.

9.5.5 Amon Sampler Deployment Period

AMoN samplers should be deployed for 14 days (336 hours), but other deployment periods may occur due to operators’ schedules, holidays, and national emergencies/shutdowns. A sampler deployed for <312 hours (1 day shorter) is coded as valid (QR=A) but will get a “s” flag for short sample period, and deployment of over 360 hours is still valid but is qualified for long sampling period (“e” flag, QR=B).

9.5.6 AMoN Travel Blanks and Duplicates

At least 25% of the AMoN sites receive travel blanks each deployment, and travel blanks are rotated across sites to ensure that all sites receive travel blanks several times per year. A travel blank is a sampler prepared and packaged in a manner identical to deployed samplers but it is labelled as a TB and the operators should not open the TB jar but store it for the deployment period and then return with the deployed sampler(s). Duplicate samplers are sent to approximately 15% of the sites also in a rotating fashion. The Wisconsin Arboretum site (WI06, UW Arboretum) will be sent a travel blank and a duplicate every deployment as an additional QC check.

9.5.7 Low-Ammonia Sample Processing Environment

AMoN passive samplers are prepared and extracted in an ammonia scrubbing hood in a dedicated processing room containing two ammonia scrubbing hoods and an ammonia scrubbing floor unit designed to significantly lower ambient levels of ammonia in the air. Hood filters (acid-impregnated carbon, backed-up by a HEPA) are replaced approximately every 12 -18 months to ensure ammonia scrubbing capability. This is recorded here: O:\Teams\NADP\NADP Lab\Equipment\Ammonia Hood Filter Tracking.xlsx. Ammonia levels are monitored by deploying AMoN passive samplers in the room and hoods for two-week periods. An extraction hood blank is deployed during every extraction day from the beginning until end of extraction. If hood or room blanks are trending high, then the hood filters may need replacing sooner.

9.6 MDN Sample Receiving and Processing

MDN samples for total mercury (HgT) and methyl mercury (MeHg) analysis are received at HM, logged into the MDN LIMS, assessed for open bags, leaks (pH checks on water in the bag), and sample weights are obtained. Methyl mercury subsamples are taken from applicable sites. Samples are sent via shuttle to AG for preparation and analysis. MDN samples are collected at each site on a weekly schedule.

9.6.1 MDN Sample Processing

MDN samples are sent to AG from HM after login. At AG they are oxidized or distilled and then analyzed. The excess sample is saved until sample data packets are Peer reviewed, uploaded to LIMS and the lab manager has checked for missing sample results.

9.6.2 MDN Sample Preservation

Samples are collected in the field directly into acid (1% v/v HCl) pre-charged PETG bottles and thus mercury is stabilized immediately upon collection.

9.6.3 MDN Sample Volume Assessment

Sample volumes less than 1.5 mL are considered dry and are not analyzed for total mercury. Sample volumes greater than 1.5 mL are analyzed for total mercury and if the volume is greater than 25 mL a split for methyl mercury may be taken (if the site is one of the select MeHg required sites).

9.6.4 MDN Hold Time

MDN analyses are to be completed within 2 months of arrival at the HAL. Refer to Table 3 above for network sample details.

9.6.5 MDN Sample Collection Deployment Period

MDN sample bottles should be deployed for 7 days (168 hours), but other deployment periods may occur due to operators' schedules, holidays, and national emergencies/shutdowns. A sampling period for > 194 is coded as invalid (QR=B).

10 Sample Chemical Analysis

10.1 Analysis Overview

Precipitation samples are typically characterized by low dissolved solids (< 20 mg/L) resulting in a poorly buffered sample. The concentrations of the NADP analytes are typically very low compared to other water samples (surface water, ground water, and wastewater) analyzed at the WSLH and therefore to avoid cross-contamination and further optimize for low level measurements, the WSLH purchased new instruments dedicated to the NADP program. In parallel, strict protocols for supply and lab cleanliness must be adhered to minimize contamination and produce the highest quality data possible. All staff wear gloves of the appropriate type when handling samples (latex must not be used for NTN), supplies that are cleaned are allowed to dry in HEPA hoods, autosamplers are covered and caution is taken when aliquoting samples.

10.2 Instrument Calibration

Each CAL instrument is calibrated daily before use. For IC, this occurs at the beginning of each run and initial calibration verification must pass before the analysis proceeds. As IC analytical sequences are very long (many runs proceed throughout the night) continuing calibration checks (CCVs) are evaluated post-run. ICP-OES and FIA instruments are calibrated and calibration verified before samples are analyzed. pH and specific conductance meters are calibrated each day and are re-calibrated if more than 4 hours has elapsed from the initial daily calibration. Each platform has a specific run sequence of quality control checks which must be successfully completed after calibration. The CAL analytical sequences are detailed in the analytical run protocols O:\Teams\NADP\NADP Lab\LAB Final Forms\Run Protocols and in the specific instrument SOPs. An example run protocol for IC is included in **Appendix H.** For mercury, CVAFS calibration is verified before samples are run and recalibrated if the ongoing precision and recovery standard (OPR) is not within the required criteria.

10.3 Analytical Quality Assurance

Quality assurance for the analytical measurement process is a multi-tiered program which includes bench-level QC, laboratory management-level QA, and participation in external QA monitoring efforts. The laboratory continually strives to improve current methods and to explore new instrumentation that will achieve optimal detection limits, improve sample throughput, enhance measurement precision, and reduce bias and interferences.

10.4 CAL Initial QC Standards

Initial QC standards are analyzed at the beginning of each analytical run. See **Appendix I** for the table outlining most of the QC standards and control limits (NTN standards FCRM and FMDL are not listed on those tables). LIMS IDs for QC standards all begin with the letter "F" due to the design of the NADP LIMS. See Acronym Table in **Appendix K** for a complete list of the QC acronyms. In the standard naming convention "L" is for low, "LP" is for low ICP-OES standard on the high curve, "M" is for mid, "B" is for blank "FR50" Is faux rain at approximately 50th percentile of field NTN

concentrations. The FL, FB, FR50 that are analyzed at the beginning of the run (after calibration) must meet acceptance criteria before analyses proceeds.

10.4.1 FL Standard (FL or FLP)

FL Description: Second source standard at low concentrations analyzed after initial calibration to confirm appropriate calibration. It must pass criteria before the run can proceed. The low level standard is usually at or close to the concentration of the lowest calibration standard. ICP-OES has two low level standards at different concentrations, the FL for the low calibration curve and the FLP for the high calibration curve. The use of both low and high calibration curves minimizes dilutions, saves sample volume and optimizes accuracy over the broad calibration range. The FL standards must be prepared from a stock that is from a different vendor (second source) and/or lot number than the calibration curve stock standard.

FL Criteria: 80-120% recovery for ICP-OES, IC and FIA; within 0.2 pH Units for pH and 95-105% for conductivity.

FL Corrective Action: The run must be stopped and the issue assessed/resolved. Recalibrate and reanalyze the FL. If the FL continues to fail, then a new FL standard should be prepared (check stock concentration and mixing volumes). Samples must be associated with a passing FL.

10.4.2 FR50 Standard

FR50 Description: A faux rain standard mix with all NTN and AMoN analytes at approximately the historical 50th percentile of NTN sample concentrations (50^{th} percentiles determined prior to 2018). Prepared by the CAL in large batches.

FR50 Criteria: 90-110% recovery ICP-OES, IC and FIA; within 0.2 pH units for pH and within 1.0 µS/cm for conductivity.

FR50 Corrective Action: the run is stopped and the issue assessed. Re-calibration or reanalysis of the FR50 should be done. If the FR50 continues to fail, then a new standard should be prepared. Samples must be associated with a passing FR50 or qualified.

10.4.3 FCRM Standard

FCRM Description: in-house or purchased certified reference material (sometimes leftover proficiency test samples are utilized) with a known true value or most probable value.

FCRM Criteria: 85-115% recovery (based on true value) or +/- NTN MDL whichever is greater. Not analyzed for pH or conductivity.

FCRM Corrective Action: this is an ongoing QC tool and does not require immediate corrective action if control limits are exceeded. This is a tool used by the QA Manager to monitor analytical shifts, change in bias and as an extra QC tool for the analysts when experiencing other QC issues.

10.4.4 FMDL Standard

FMDL Description: A faux rain standard mix at 2-5 times expected MDL_N concentrations. This is analyzed with each batch of samples primarily for the purpose of calculating new laboratory MDLs

and to assess ongoing analytical performance at low concentrations. This is prepared completely separately from the FR50. It also includes phosphorus which the FR50 does not.

FMDL Criteria: 80-120% recovery or +/- NTN MDL whichever is greater. Not analyzed for pH or conductivity.

FMDL Corrective Action: this is an ongoing QC tool and does not require immediate corrective action if control limits are exceeded. This is a tool used by the QA Manager to calculate analytical MDLs, monitor analytical shifts, change in bias and as an extra QC tool for the analysts when experiencing other QC issues.

10.5 CAL Batch QC Standards

Batch QC is analyzed within each analytical sequence (batch) at a frequency of after every 10 NTN or AMoN samples. See **Appendix H** for an example of IC batch QC. All analytical QC failures are noted on data packets and also the qualifier sheet if the sample cannot be successfully rerun.

10.5.1 FM Standard

FM Description: mid-calibration-level concentration standard – run every 10 samples and must pass criteria. If samples are not bracketed by passing FM check standards, then that group of samples must be rerun.

FM Criteria: 90-110% recovery ICP-OES, IC and FIA; within ±0.2 pH Unit, and 95-105% recovery for conductivity.

FM Corrective Action: Each set of 10 samples must be bracketed by an acceptable FM standard for each analyte. If the FM does not meet the criteria then those samples (and duplicates) that are not bracketed by an acceptable FM must be rerun or qualified if rerun is not possible.

10.5.2 FB Standard

FB Description: analytical blank consisting of Type I water analyzed every 10 samples except for pH analysis.

FB Criteria: $\pm MDL_N$ for ICP-OES, IC and FIA; <1.0 µS/cm for conductivity (does not apply to pH).

FB Corrective Action: Each set of 10 samples must be bracketed by an acceptable FB for each analyte or be rerun or qualified on the possible qualifiers table. Source of contamination must be investigated and resolved.

10.5.3 Analytical Sample Duplicate

Analytical Sample Duplicate Description: a second sample aliquot is analyzed later in the batch (normally not adjacent to the original) and the precision between the two results is evaluated. A duplicate is chosen at random (volume permitting) and one duplicate must be analyzed for each group of 10 or less samples.

Duplicate Criteria – duplicates are assessed based on the network MDL for that calendar year. Criteria

are dependent upon sample concentration (see Table 4 for specifics).

Duplicate Corrective Action: Each set of 10 samples must be bracketed by an acceptable duplicate for each analyte or be rerun or qualified on the possible qualifiers table.

TABLE 4. Duplicate Assessment Based on Concentration – Network MDL is used for all criteria

Sample Result	Duplicate Result	Calculation	Criteria
MDL to 10 x MDL	MDL to 10 x MDL	Absolute Difference (AD)	-MDL<AD< +++MDL
"n.a." (IC only)	> MDL	AD (with ½ MDL substituted for n.a.)	-MDL<AD< +MDL
< MDL	< MDL	AD = ND (Absolute Difference = No Difference)	None
< 10 x MDL	> 10 x MDL	AD or RPD	-MDL<AD< +MDL or RPD within ±10%
> 10 x MDL	> 10 x MDL	RPD	Must be within ±10%

10.6 CAL Linear Dynamic Range and Carryover Determination

10.6.1 LDR

LDR Description: the linear dynamic range is determined when a new instrument is acquired or a major method change occurs. One test, repeated on two separate days, can fulfill the purpose of both the linear dynamic range and carryover determinations. Linear dynamic range (LDR) is defined as the highest concentration in which the standard recovery is within 90 to 110% of the true concentration value. To determine this, the chemist will prepare a series of low to high concentration standards starting above the highest calibration standard. For example: if the calibration curve's highest standard is 2.0 mg/L, the chemist may prepare 5, 10, 15, 20 and 25 mg/L standards. After the instrument has been calibrated and all initial QC has passed, then these standards will be analyzed with a blank between each standard.

LDR Criteria: all the recoveries of standards between 90 to 110% are acceptable – the standard at which this fails to be met is above the LDR so the next highest standard is set as the LDR concentration. For example, if all standards in the series above met the 90-110% recovery except the 25 mg/L standard, then the LDR would be determined as MDL -20 mg/L for that analyte.

Application of LDR: During an analytical run, if a sample value is greater than the top calibration standard and there is insufficient sample volume available to perform a dilution to bring the response back within the calibration curve, the non-diluted value may be reported if it falls within the determined LDR (20 mg/L from the above example). The sample value would still be noted on the "possible qualifier" spreadsheet (O:\Teams\NADP\NADP Lab\Possible data qualifiers), but would be considered a valid sample result. If the non-diluted value exceeds the determined LDR and cannot be diluted then the value will not be reported.

10.6.2 Carryover

Carryover Description: the carryover concentration is determined when a new instrument is acquired or a major method change occurs. Carryover is defined as analyte from a sample/standard which impacts the next sample in the analytical sequence at a concentration greater than the MDL_N. To

determine this, the LDR protocol can be used simultaneously to determine the impact of high concentrations on blanks.

Carryover Criteria: any blanks >MDL_N indicate carryover at that concentration. For example: If the blanks that follow the 5 mg/L and 10 mg/L standards are below the MDL, but the blank which follows the 15 mg/L standard is greater than the MDL, then the determined carryover limit would be 10 mg/L.

Application of Carryover: During an analytical run, if a sample value is greater than the determined carryover limit (10 mg/L in the above example) then the sample following this must be rerun to confirm there was no carryover impact from the previous high sample concentration. If a sample concentration is above the highest calibration standard but falls within the acceptable determined carryover range (i.e. less than 10 mg/L) then the following sample does not need to be rerun. If a sample that has been potentially compromised by high sample preceding it, then it will be rerun. If it cannot be rerun it will be listed in the potential qualifiers sheet.

10.7 HAL Analytical QC

HAL QC samples are analyzed within each analytical sequence. See **Appendix I** for HAL criterion table. With the exception of calibration standards, LIMS IDs for QC standards all begin with F due to the design of the NADP LIMS.

10.7.1 Calibration Blanks (FCB)

FCB Description: Three calibration blanks, prepared with reagents in proportions similar to samples (0.5% HCl (v/v) and 1% BrCl (v/v)) are analyzed before each calibration. The mean peak area of the calibration blanks is subtracted from every calibrator, QC, and sample result as a blank correction.

FCB Criteria: The mean concentration of the three blanks must be <0.5 ng/L for Total Hg and ≤0.05 ng/L for Methyl Mercury per the reference method. The standard deviation of the blanks for Total Hg must be less than 0.1 ng/L.

FCB Corrective Action: The run must be stopped and the issue assessed/resolved. If the concentration is high, reagent components of the FCB should be checked for purity. If the standard deviation is high, the system should be cleaned and retested.

10.7.2 Calibration Standards (not tracked in LIMS due to lack of such function)

Calibration Description: A calibration is not required to be analyzed daily. If a calibration is not run, the batch must be preceded by a 5 ng/L calibration check (initial OPR) that is recovered in the range of 90%-110%. If the calibration check does not meet this criterion, a new calibration must be run. Five calibration standards are analyzed in the range of 0.5 ng/L – 100 ng/L for Total Mercury and 0.1 ng/L – 3.6 ng/L for Methyl Mercury. A calibration factor is calculated from each of the five standards by dividing blank corrected peak area by the theoretical standard concentration. The mean of the calibration factors is used for calculating results.

Calibration Criteria: Each of the calibration standards must be recovered in the range of 85%-115% for Total Mercury and 65%-135% for Methyl Mercury per the reference methods. These limits will be re-assessed and possibly changed after enough QC data has been collected. The relative standard

deviation of the calibration factors must be ≤15% for Total and Methyl Mercury.

Calibration Corrective Action: The run must be stopped and the issue assessed/resolved. Accuracy of pipettes used for delivery of standards should be confirmed and the system cleaned and retested.

10.7.3 Continuing Calibration Blanks (FCCB)

FCCB Description: Identical in composition to FCB, these analytical blank checks are performed after the calibration and after every ten samples.

FCCB Criterion: The concentration must be less than the MDL.

FCCB Corrective Action: The run must be stopped and the issue assessed/resolved. The system is cleaned and retested.

10.7.4 Ongoing Precision and Recovery (FOPR)

FOPR Description: A calibration check at 5 ng/L for Total Mercury or 0.3 ng/L for Methyl Mercury, using the same source as the calibration standards. This is analyzed at the beginning of the sample sequence and after each set of 10 samples.

FOPR Criterion: The FOPR must be recovered in the range of 80%-120% for Total Mercury and 65%-135% for Methyl Mercury. If more than 12 hours have passed since the last FOPR was analyzed, this calibration check must be recovered in the range of 90%-110% for HgT.

FOPR Corrective Action: The run must be stopped and the issue assessed/resolved. Another FOPR may be analyzed. If a second FOPR fails, the system should be cleaned and tested. If no cause can be found, the system must be recalibrated.

10.7.5 Ongoing Method Detection Limit Verification (FMDL)

FMDL Description: A spiked solution in Type I reagent water prepared at 0.5 ng/L using the same source as the calibration standards. It receives 0.5% HCl (v/v) and 1% BrCl (v/v).An aliquot of this solution is delivered to vials and analyzed identically to samples with each batch to collect long term data on instrument sensitivity and repeatability. These standards are used to generate or verify the lab MDL.

FMDL Criteria: There are no criteria for this control that affect the acceptability of a specific batch, but extreme deviation from the expected value should cause the analyst to scrutinize other performance controls.

FMDL Corrective Action: No corrective action is required. When these are assessed annually, a change in the MDL may be prompted.

10.8 HAL Batch QC

Batch QC is prepared and analyzed with each analytical sequence (batch) of samples to confirm that reagent process blanks and calibration are in control and that sample pre-treatment results in acceptable analyte recovery. Every control group of ten samples or fewer is accompanied by one MS/MSD pair and bracketed by an OPR and CCB. If the MS/MSD fails, only the affected control group must be reanalyzed. If the OPR or CCB fails, any control group that it brackets (up to twenty samples) must be reanalyzed.

Except for the Matrix Spikes, batch QC LIMS IDs begin with F due to the design of the NADP LIMS.

10.8.1 Digested Laboratory Reagent Blanks (FLRB)

FLRB Description: Three procedural blanks are assigned to each sample batch.–They are prepared with Type I reagent water and receive 0.5% HCl (v/v) and 1% BrCl (v/v) at the time that samples in the batch are oxidized with BrCl.

FLRB Criterion: The concentration must be less than the MDL.

FLRB Corrective Action: The run must be stopped and the issue assessed/resolved. If the system is clean and reanalysis of the reagent blanks still yields high results, the source of contamination is investigated. If the BrCl is determined to be the source the batch is considered contaminated and sample results should be flagged. Samples needing flagging are added to the possible qualifiers table and data review staff add notes to LIMS,

10.8.2 Digested Quality Control Standard (FQCS)

FQCS Description: A second source mercury stock standard (other than the calibration standard) is used to prepare (with Type I reagent water) check solutions at 8 ng/L for Total Mercury and 1 ng/L for Methyl Mercury and treated with BrCl alongside the assigned sample batch.

FQCS Criterion: The FQCS must be recovered in the range of 80%-120% for Total Mercury and 65%-135% for Methyl Mercury.

FQCS Corrective Action: The run must be stopped and the issue assessed/ and resolved. If the system is clean and reanalysis of the FQCS still yields results out of range, the source standard should be tested directly. If the source standard response is appropriate and there is no obvious source of error or contamination in the preparation step, the sample results should be flagged.

10.8.3 Matrix Spikes and Matrix Spike Duplicates

10.8.4 (MS and MSD are not tracked in LIMS but are tracked in spreadsheet O:\Teams\NADP\NADP Lab\HAL\HAL QA\MDN MSMSD Tracking.xls)

MS/MSD Description: Sample spikes (MS) and sample spike duplicates (MSD) are prepared at a frequency of 10% of sample batch size. Higher volume samples are randomly chosen for MS/MSD so that there is enough volume for potential reruns. The samples are spiked identically at 15 ng/L for Total Mercury and 0.5 ng/L for Methyl Mercury.

MS/MSD Criteria: The recovery of the spikes must be in the range of 75%-125% for Total Mercury and 65%-135% for Methyl Mercury. The absolute percent difference of the replicates (MS and MSD) must be ≤24% for Total Mercury and ≤35% for Methyl Mercury. These limits are set by the reference methods and will be reassessed when enough data has been accumulated.

MS/MSD Corrective Action: The run should be stopped and the issue assessed/resolved. The MS/MSD should be prepared and analyzed again. Test the source of standard used for spiking. If precision is acceptable but accuracy remains out of range, this may be attributed to matrix effects. Any control group of ten samples with a failing MS/MSD pair must be reanalyzed, even if bracketing instrument checks

are acceptable.

10.9 Uploading CAL/HAL QC results to the LIMS

All analytical QC samples are uploaded to the LIMS and can be accessed/viewed via control charts within Benchchem LIMS. Calibration standards, failed NTN/AMoN duplicates/dilutions, and MDN MS/MSDs are not uploaded to LIMs. Instead, they are recorded in the data packets and/or external spreadsheets as applicable. Failed duplicates/dilutions are not uploaded to LIMS due to the possibility of accidentally reporting the invalid sample data. These issues are noted on the possible qualifiers spreadsheet as well as on the relevant data packet. Duplicate failures are tracked on a shared spreadsheet which the QA Manager reviews at least quarterly (O:\Teams\NADP\NADP Lab\QC failures\Duplicate Failures.xls).

11 Method Detection Limits (MDLs)

Refer to **Appendix D** for the 2018-2020 MDLs. Now that the laboratories are established at the WSLH new MDLs will be calculated each year and compared with previous years MDLs. MDLs will generally not be changed if the new MDL is within 0.5 times the established MDL and less than 3% of the method blanks are above the established MDL. Method blanks are those analyzed daily on analytical sequences. If over 3% of blanks are above the MDL for that period of data assessment the MDLs should be updated to the highest newly calculated MDL.

11.1 NTN Laboratory MDLs

11.1.1 MDL_L Spike Calculations

The analytical **laboratory** method detection limit (MDL_L) is the minimum measured concentration of a substance that can be reported with a 99 percent confidence that the measured concentration is distinguishable from method blank results. The MDL_L is based on the absolute standard deviation from a minimum of seven measurements (analyzed on different days) of spiked samples in the matrix of concern at a concentration of approximately 2-5 times the estimated network MDL. The MDL_L for the MDL solution (clean spike mix run daily) is calculated following the standard federal protocol from 40 CFR part 136, Append. B and is calculated as sample standard deviation * t value at 99% confidence level. All valid MDL standard data available for the previous year is used to do this calculation. MDL samples (FMDL) associated with other QC/calibration issues on a particular day may be excluded. This can also be assessed over time to identify any trends over the year.

11.1.2 MDL_L Blank calculations

A minimum of seven calibration blanks are also assessed to determine a lab MDL based on blank measurements (per 40 CFR 136). A Type I water blank is analyzed with each batch of samples on each instrument (pH is the only exception). The blank MDL will be determined using the mean of the blanks + blank standard deviation * t value at 99% confidence per federal MDL protocols. The MDL based on the blanks should be used as the analytical lab MDL if the result is greater than the spiked lab MDL result. All valid blank (FB) data available for the previous 6-12 months is used to do this calculation. Blanks associated with other QC/calibration issues on a particular day may be excluded. The FBs can also be assessed more frequently using this process to identify any trends over the year.

11.1.3 MDL_L Usage

The QA Manager compiles the daily QC MDL spike solution (not processed through the NTN buckets as is the MDL_N – see below) and daily blank results from the previous 6-12 months and utilizes those data for laboratory MDL calculations. Analytical **laboratory** MDLs are a data quality indicator and are reviewed annually by the CAL Management Team and revised by the QA Manager as warranted (i.e. a new instrument or a critical new part is installed on an existing instrument). The analytical **laboratory** MDL is primarily used to validate instruments and is used as a tool for the QA Manager to assess the Network MDLs validity. It is not used for qualifying NTN data.

11.2 NTN Network MDLs

11.2.1 Network MDL Process

The network specific MDL (MDL_N) for NTN is based on results from a minimum of 7 MDL solutions (spikes) or Type I water (blanks) which go through all processing steps and are analyzed with other samples. The network MDL accounts for variability in results on the low end due to exposure to sample collection equipment and processing.

The MDL solution is the same as that used for MDL_L analyses with analyte concentrations set to approximately 2-5 times the previously established MDL_N. The calculations are the same as those used to determine the MDL_L described above using the USEPA protocol for either spikes or blanks. The difference is that the network spikes or blanks go through the entire process (i.e. bucket exposure, filtering and transferring to bottles) and are blind to the bench chemists.

To create an MDL_N sample a ~100-150 mL aliquot of the current MDL solution (the same solution that is used for MDL_L) or Type I water is poured into a clean NTN bucket, covered with a clean lid and left in the lab at least overnight. The next day the solution is poured into a used clean NTN 1 liter bottle. Later that day (or the next day) the NTN MDL sample is filtered into a standard 60 mL bottle, stored at 4°C and sent to the lab for analysis. Ideally, all MDL verification samples prepared this way will occur on separate weeks with different NTN supplies used in the preparation. The resulting network MDLs are assessed and if the new network MDL results are less than 0.5 times the previous year, the MDL values may remain the same for another year.

11.2.2 Network MDL_N Usage

When enough data points have been generated (minimum of 7 but ideally 15 or more) the QA Manager will calculate the network MDL for the following year. Due to the transition process, the 2018 WSLH NTN MDLs were those listed in the Readiness Verification Plan Final Revision (approved by the QAAG in spring of 2018). For 2019, the NTN MDL_N results from 20 MDL_N samples were used to calculate the MDL_N. For 2020 MDLs, this verification became complicated due to use of the 2019 NTN MDL solution to model the anticipated change in NTN sampling from buckets to bag-lined buckets. Losses of ammonia, nitrate, and phosphorus from some of the MDL spike solutions resulted in very high standard deviations and unacceptable MDLs for some analytes. Blanks were then put through the NTN MDL processes to generate more data. A combination of the blank and the MDL solution data (processed using sampling bags) was then used to assess the network MDLs and verify that the MDLs established in 2019 could be used for 2020. The bag analyte loss issue is still being investigated, and the network is continuing to use buckets for the majority of the sites. Therefore, MDLs based on buckets for 2019 will be applied to 2020 data.

The MDL_N is used to censor NTN data published by the PO for samples received in the calendar year. The sample IDs for that calendar year are documented in the Historical MDL table (**Appendix D**). The NTN sample results that are less than the MDL_N for that calendar year are published on the NADP website with the MDL_N value in place of the measured value and a less than (<) symbol in the column adjacent to the result. AIRMoN sample results were published even if the result is below the MDL_N because it was considered a research network. Individual site operators and sponsors receive the uncensored values on their preliminary reports regardless of the network or MDL. For NTN, the data reported to the sites is italicized if it is less than the NTN MDL_N for that calendar year.

11.3 AMoN Lab MDL (MDL_L)

The AMoN Lab MDL (MDL_L) is used for bench level QC (e.g. assessing blank acceptability, establishing low level standard values, and identifying samples <10*MDL). The AMoN MDL_L is also used to flag travel blanks less than the MDL_L with a d flag and results in a QR of B. See **Appendix D** for a list of AMoN MDLs.

In 2018, the CAL utilized the ammonium NTN lab MDL as the AMoN MDL due to the similar analytical platforms and a lack of core data to use to generate a true AMoN MDL.

In 2019, the AMoN MDL_L was set equal to the mean core blank value from June – December 2018 = 0.016 mg/L. This MDL_L reflects the variability in the background ammonia present in the core prior to deployment.

In 2020, the AMoN Lab MDL is equal to the mean core blank value for all available core blanks with results greater than zero. There were 103 core blank values from June 2018 – December 2019 used to determine a mean of 0.013 mg/L NH_4 to be used as the MDL_L.

11.4 AMoN Network MDLs

11.4.1 AMoN MDL_N Calculations

The network specific AMoN method detection limit (AMoN MDL_N) will be calculated annually from valid travel blanks (coded with quality rating A or B – see **Appendix G**). Travel blanks are AMoN samplers prepared in the same manner as the deployed samplers that are shipped to individual sites but are not opened or deployed in the field. All other laboratory handling and extractions of travel blanks are identical to the deployed samplers. Approximately 25% of sites receive travel blanks on a rotating basis with each bimonthly deployment. This currently equates to over 700 travel blank data points per year. AMoN Network Detection limits are calculated by pooling all valid travel blank (TB) data available in final format and using the mean to calculate an MDL_N based on the federally promulgated MDL protocols (40 CFR Part 136) for blanks. The MDL_N is the mean of all valid travel blanks plus the sample standard deviation (s) * the t value at the 99% confidence level. AMoN MDL_N = mean valid travel blanks + ($s * t^{99}$). See **Appendix D** for a list of AMoN MDLs.

11.4.2 Annual AMoN MDL_N

Prior to 2018

AMoN data prior to 2018 was assessed and flagged by the former CAL and PO based on a historical MDL_N of 0.04961 mg/L (unknown origin of this MDL).

AMoN MDL_N 2018
The WSLH obtained the ISWS 2017 valid travel blank data in order to calculate the 2018 MDL_N for AMoN which was 0.119 mg/L NH_4.

AMoN MDL_N 2019
The 2019 AMoN MDL_N was calculated using all valid 2018 travel blanks. Travel blank data from January through June was from ISWS analysis while June through December data were WSLH data. The 2019 MDL_N was calculated from 636 valid travel blanks and was 0.104 mg/L NH_4.

AMoN MDL_N 2020
The 2020 AMoN MDL_N was calculated using all valid travel blanks for approximately 12 months of the most recent samples for which final data was available. The 2020 MDL_N was calculated from 741 valid travel blanks with "end dates" (end of deployment period) from June 2018 to June 2019 and is 0.083 mg/L NH_4.

11.4.3 Use of AMoN MDL_N for data assessment

The AMoN Network MDL is used to flag data that is below the MDL_N with a "d" which automatically changes the sample QR code from "A" to "B". Other factors could further reduce the QR to a "C" (Refer to AMoN notes code information in **Appendix G**). AMoN data is reported with a QR code and is not "censored" to the MDL_N.

11.5 AMoN Travel Blank Assessment

Travel blanks will be critically assessed every quarter. The AMoN analyst also assesses travel blanks every analysis week and will alert the QA Manager of any concentrations that exceed criteria. If a significant increase in the travel blank concentrations suggests a network wide shift in AMoN baseline concentrations, then the QAAG and PO will be consulted. If the increase in travel blanks is determined to be of concern, then all potentially affected data may be flagged before it is reported to the PO. This would likely be flagged using an "h" flag which covers field and lab issues and would result in the data having a QR code of "B". As in the past, travel blanks with measured results over 0.2 mg/L NH_4 will be flagged with a "t". The travel blank criteria of 0.2 mg/L NH_4 was carried over from the previous CAL (unknown origin). The associated deployed samples from a set, which can include 1-3 samples if the site received duplicates or triplicates, historically have not been flagged because only 25% of sites per deployment have a travel blank.

11.6 MDN MDLs

11.6.1 MDN mercury MDLs for waters are calculated according to EHD QA 116 SOP and 40 CFR Part 136, Appendix B, using only spiked reagent solutions prepared in the laboratory.

11.6.2 MDN MDL Establishment

11.6.3 Initially, a minimum of seven method blanks and seven spiked samples are prepared and analyzed over three days. The spiked sample concentration is prepared at 1-5 times the estimated MDL, using a second-source standard. Both blank and spike samples are prepared in-bottles with all reagents that are used to prep and analyze natural matrix samples. The MDL of spikes is calculated by multiplying the standard deviation of the measured concentration of the spiked samples by the students' t-value at the 99th percentile. The MDL of the blanks is

calculated by multiplying the standard deviation of the measured concentrations of the blanks samples by the students' t-value at the 99th percentile and adding the mean of the blank concentrations. The selected MDL is the greater of the MDLs calculated from the blanks and spikes.

11.6.4 Ongoing MDN MDLs

11.6.5 MDLs are verified by analyzing a spiked solution, prepared with 0.5% HCl (v/v) and 1% BrCl (v/v), at a concentration between 1-5x (currently 2.5x) the initial MDL with every analytical run. Annually, these spiked samples and all of the batch method blanks are assessed. The "annual" MDL is again calculated and may remain unchanged if all of the following criteria are met: 1) the new MDL is within 2x the current established MDL, 2) fewer than 3% of the method blanks are above the established MDL, and 3) fewer than 5% of the spiked samples fail to meet recovery criteria.

11.6.6 MDN MDL Adjusted by Dilution

11.6.7 Because mercury methods for waters are pre-concentrated, the MDL changes with the volume analyzed. The standardized (maximum) volume is 30mL. If a smaller volume is used, the MDL is multiplied by the dilution factor to define the MDL for an individual sample.

12 Audits, PTs, and Corrective Actions

12.1 External Audits

Periodic on-site technical reviews are conducted to evaluate documents, activities, materials, data, and other work products that document bias, precision, completeness, and representativeness metrics of the NADP laboratories. NADP representatives and invited scientists, technicians, and IT professionals from various scientific organizations conduct on-site CAL and HAL technical reviews every three years with a follow-up report presented to the QAAG within one year after the on-site reviews per the NADP Quality Management Plan (2016).

12.2 Internal Audits

Internal audits are conducted by the QA Manager or other WSLH staff with equivalent experience and training in the systems or methods being audited. An internal systems audit which covers the overarching lab components outlined in this QAP will be conducted at least annually by the QA Manager. However, internal audits may be requested at any time by the NADP Management Team to address specific aspects of the NADP program.

Method audits will be completed at a minimum of every two years for all NADP analytical methods. Method audits are specific to each analytical method and include a review of a randomly selected data packet. Internal systems audit and method audit reports will be prepared and any findings will be reviewed with the NADP management team and corrective actions will be taken. The lab managers are responsible for making sure corrective actions are implemented. The QA Manager is responsible for retaining records that document review findings, responses, and corrective actions.

12.3 Performance Test Samples

Performance Test (PT) samples are prepared by an outside organization and laboratories contract with these PT vendors to assess accuracy of their analytical lab results. The vendors assemble the data from

the participating laboratories and establish statistically determined consensus "true" concentration values against which each laboratories performance is judged. The CAL is currently participating in three PT programs, and the HAL participates in two programs. The programs provide feedback on lab performance relative to other participating labs in the study. In most cases, true values based on the pooled results along with associated control and warning limits are provided by the PT vendor after they tabulate the results. The World Meteorological Organization (WMO) PT provider also produces a ring diagram assessment which documents and illustrates possible general laboratory bias in the data. PT results outside of the prescribed control limits will result in evaluation for corrective action and are reported on the WSLH Occurrence Management System (see Section 13.6). The QA Manager also reviews PT results on a regular basis for trends or analyte specific bias.

After the PT true values are obtained from the outside provider the PTs may also be utilized as internal blinds for DOCs or CRMs for performance monitoring. WMO and ECCC PTs (See Table 5) are transferred to 60 mL bottles and sent through the normal QC sample login process. The PTs are single blind samples for the laboratory as their status, but not concentrations, as PT samples is known. The WMO/ECCC samples are double blind to the analysts whereby their PT status is masked. All PT samples are analyzed in the same manner as normal natural matrix NADP program samples.

The NADP is not aware of a PT program for ambient air sampling of ammonia, therefore the CAL will utilize previously analyzed ammonium PTs (used for NTN) as surrogate AMoN PT samples which will be matrix matched and analyzed on the AMoN FIA instrument twice a year.

The laboratories are always on the look-out for relevant PT programs, CRMs and inter-laboratory comparisons to provide additional external assessments of NADP data accuracy.

TABLE 5. PT Providers

PT Provider	CAL ID #	Study Timeframe	Name of PT	Analytes Possible	# of samples/ event & volume
ECCC	F303	2 X per year NTN, 1x Year MDN Jan/ August	RN - Rain and Soft Water, LLHg	Acidity, alkalinity, aluminum, ammonia, calcium, chloride, conductivity, magnesium, nitrate, pH, potassium, sodium, sulfate, total nitrogen, total mercury	10 - 500 mL NTN, 4 MDN
WMO	700175	2 X per year May/Oct for NTN	WMO/GAW Simulated Rain	pH, conductivity, sulfate, nitrate, chloride, ammonium, sodium, potassium, calcium, magnesium, fluoride, and acidity (no orthophosphate	3 - 250 mL
USGS	NA	Monthly	USGS Inter-comparison	Ammonium, calcium, chloride, conductivity, magnesium, nitrate, pH, potassium, sodium, sulfate, orthophosphate, total mercury	4 - 60 mL NTN, 2 MDN

USGS PT Website = https://bqs.usgs.gov/precip/mdn_interlab_overview.php
WMO PT Website = http://www.qasac-americas.org/study-results

12.4 Occurrence Management Reports

The Wisconsin State Laboratory of Hygiene utilizes "Footprints" software for tracking Occurrence Management (OM) Reports. Examples of occurrences entered are PT failures, equipment issues, customer complaints, reporting errors, etc. The WSLH internal web site includes a link to the Footprints software for Occurrence Management Reports.

There are two lab-wide SOPs that document the use of Occurrence Management forms:
LABWIDE GENOP 706, Occurrence Reporting Procedure
LABWIDE GENOP 707, Occurrence Management System Policy

Whenever possible, supporting documentation is linked to the OM form in the attachment tab. Documentation of occurrences must be made either by the person who discovered the problem, their supervisor, or the QA Manager. Documentation of the occurrence must be made within a week of the discovery of the occurrence. Follow-up action, monitoring results, and root cause analysis must be documented within the OM form. Occurrences are discussed at staff meetings on at least a quarterly basis to minimize similar occurrences and assist in educating all staff. Annually, occurrences are also categorized to assess for possible systematic issues.

12.5 Corrective and Preventative Action

12.5.1 Corrective Action

Generally, when any aspect of sample testing does not conform to SOPs (nonconforming work), including QC procedures, corrective action will be initiated, including a root cause analysis and documentation of the occurrence. Corrective action requirements for analytical run occurrences can be found in Section 11 and in the analytical SOPs. Corrective action will be performed by the analyst in consultation with the peer review auditor, QA Manager and Lab Manager. The Lab Manager is responsible for management and evaluation of non-conforming work in consultation with the QA Manager. The Lab Manager is responsible for halting work or withholding test reports if deemed necessary and will authorize resumption of work. If a data error is discovered after the report has been released, the client will be notified as soon as possible and an amended preliminary report will be released when the issue has been resolved. The PO will be notified of the reissuance of any preliminary reports and changes to the database preliminary data. All communications with clients will be documented and archived using e-mail, written records, and Occurrence Management Reports (through Footprints software). If the non-conformance of work casts doubts on the laboratory's compliance with NADP policies and procedures, then the QAAG will be advised and corrective action, potentially including an internal or external audit will be taken.

12.5.2 Preventative Action

Preventative action is an essential component of QA and critical for providing accurate, reproducible, and reliable data. It ensures equipment and quality systems are functioning properly. If needed improvements or nonconformities arise, actions are taken to ensure that future occurrences are prevented. Use of the Occurrence Management Report will allow for the identification and implementation of further preventive actions. Preventative action is routinely implemented by the laboratory staff. Preventative action includes:

- Reviewing operational procedures
- Reviewing occurrence management forms for trends

- Discussing occurrences with all lab staff
- Reviewing QC data for trends and outliers
- Conducting periodic instrument maintenance
- Reviewing instrument logs for problems
- Reviewing customer (internal & external) comments and complaints
- Reviewing PT results
- Reviewing staffing and training needs
- Performing DOCs

13 Data Review

13.1 Analytical Data Peer Review

All primary analytical data is reviewed by another NADP staff person who is familiar with the analysis and QC requirements before it is uploaded to LIMS (except pH and conductivity which are recorded in LIMS in real time and reviewed later). Data review is documented on the Peer Review Cover Sheet which accompanies the data packet for each analytical run. Data review includes checking that: information on the cover sheet is accurate and complete (standard IDs, pipette IDs etc.), calibration data meets required criteria, initial QC samples meet criteria, each batch of samples (maximum of 10) are bracketed by the proper acceptable QC samples and duplicate, and continuing QC samples and duplicates are reviewed to confirm the specified control limits have been met. Over range (above the top calibration standard) samples are marked as needing dilution, and proper documentation of corrective action procedures are included. The reviewer also makes sure LDR or carryover limits are not exceeded. Samples in batches that do not meet the appropriate criteria are noted, not approved for LIMS upload and are reanalyzed as soon as possible. If there is insufficient sample remaining to reanalyze, the sample is qualified on the possible data qualifiers spreadsheet. See ***NADP SOP 202 Analytical Peer Review Process***.

Data packets for CVAFS, ICP, FIA and IC must contain:

- Peer Review Cover Sheet
- Raw data file from the instrument (including calibration coefficients)
    - For ICP this is not possible, but the Peer Reviewer reviews the electronic file
- Final data spreadsheet for upload to LIMS
- Report/spreadsheet with calculations (duplicates, dilutions etc.) and all results

13.1.1 pH and conductivity data packets must include:

- Peer Review Cover Sheet
- Spreadsheet printout of the sample analysis results for that day copied and pasted from LIMS and containing QC results as well as samples.

13.2 LIMS and Data Calculations

13.2.1 LIMS Upload

NADP sample and QC sample results are entered into the NADP LIMS via upload from the analyst computer station after the peer review process has been completed. Conductivity and pH data are transferred directly to the LIMS from the instruments. Some data calculations are housed within LIMS

and are performed when results are published to the PO. This is the case for the ammonium to ammonia conversion for AMoN as well as the application of dilution factors for samples diluted upon receipt of the type WI or WD (see section 9.3). Unlike the WI/WD dilution factors, the NTN analytical dilution factors are applied at the instrument and do not currently display in LIMS except for MDN. MDN dilution factors are applied at the instrument but are also stored in the LIMS and used to adjust the MDL for each sample.

13.2.2 LIMS Compare Review

In addition to the peer review process, the first data packets of the month for each platform are copied and provided to a chemist for LIMS compare review. This review entails a comparison of the LIMS values with the values in the raw data packet, with a focus on WI/WD samples, duplicates, dilutions and reruns. At least 4 samples from beginning middle and end of the analytical run are assessed. Issues with data are brought to the attention of the QA Manager and/or Lab Manager and corrective actions taken. This review is documented on the spreadsheet located here: O:\Teams\NADP\NADP Lab\LIMS Compare Review\LIMS Compare Review.xls.

13.3 Network Data Review

Prior to releasing reports to sites or publishing data to the PO, the CAL/HAL data managers review all NADP sample data for completeness and consistency. This includes comparison to historical site values. This review includes:

- Date and time of sample collection
- Site ID, operator initials and field form operator notes/comments
- Field equipment status, sample conditions and potential contamination
- Electronic rain gage precipitation data/Belfort chart data
- Precipitation collector sample weight and respective sample volume
- Receiving laboratory sample observations (assessment of contamination)
- pH/conductivity values
- Chemistry laboratory analysis values
- Sample data error flags
- Screening level (SL) and sample protocol (SP) coding
- Overall sample validity and determination of Quality Rating (QR) (See **Appendix G** for Notes Codes Tables)

13.4 NTN and MDN Data Review Process Overview

13.4.1 NTN/MDN First data entry

- Sample receiving staff enter field form (FORF/MORF) information into LIMS.

13.4.2 NTN/MDN Second data entry

- Different staff from 1st entry (if possible) perform a replicate round of data entry

from the field form for quality control purposes.

13.4.3 NTN/MDN Compare Report Review

- Compare 1st and 2nd data entry in database and reconcile differences.
- For each daily packet of field forms, the sample range, analyst initials and dates of 1st data entry and 2nd data entry are recorded on cover sheet.
- Second data entry and Compare Report Review are recorded on a cover sheet that is attached to each packet of field forms.

13.4.4 NTN/MDN Preliminary Screening Review

- Field form is checked for completeness and correctness of information in the LIMS. Data reviewer identifies where there are large gaps/overlaps in sampling dates, times. They also review for missing site operation or sample condition data.
- Items checked include initials, dates, times, site conditions, sample information, potential contamination, and field notes.

13.4.5 NTN/MDN Final Review

- All sample related data is verified.
- This includes electronic rain gage precipitation records, Belfort charts, chemistry results, data flags and SP/SL coding, analysis of chemistry data sample qualifiers, and overview of error flag reports.
- Any major sample or data discrepancies are resolved.
- Data review staff communicate with receiving lab staff, site operators, site liaison, and analytical staff as needed to resolve any issues.
- These communications are recorded in O:\Teams\NADP\NADP Lab\Data and Site Support\Data Review Logs\Data Review Logs (there is a log for AMoN. NTN and MDN).
- Sample Quality Rating (QR) codes are confirmed for validity.
- Review of site info, date range, field notes, contamination coding, sample volume vs rain gage comparison, daily precipitation amounts, accurate chemistry analytical values, and all other flags to verify the correct QR code has been applied.

13.4.6 Generate reports

- Preliminary reports are sent to sites.

13.4.7 Published data

- Final data from the CAL/HAL are sent to the PO.
- Data are published to the PO approximately 90-120 days from the end of sample

receipt month.

13.5 AMoN Data Review Process Overview

13.5.1 AMoN First data entry

- CAL receiving staff enters field form information into LIMS.

13.5.2 AMoN Review Report

- Similar to "Compare Report" review in other networks.
- AMoN currently has only first data entry so this is a second check on the field data.
- Verify site ID and operator initials, sample collection dates/times, and operator field comments.
- For each daily packet of field forms, the sample range, analyst initials and date of First data entry and Review Report are recorded on a cover sheet that is attached to each packet of field forms.

13.5.3 AMoN Preliminary Review

- Field form: confirm site conditions, sample information, contamination, and field notes.

13.5.4 AMoN Final Review

- Chemistry results, address analytical notes, data flags (See **Appendix G**) and coding.
- Resolve any major discrepancies with data or sample records.
- Completed through communication with site operators, receiving lab, analytical lab, and site liaison as needed.
- Confirm all sample QR codes for validity.

13.5.5 Generate reports

- Preliminary reports are sent to sites.

13.5.6 Published data

- Final data from the CAL is sent to the PO.
- Data are published to the PO approximately 90-120 days from the end of sample receipt month.

14 Sample Archive

Current NADP sample archive procedures (previous archive policy is given in **Appendix J**)

14.1 Archive Software

WSLH CAL instituted in 2019 the use of a robust archive software program (Freezer Pro Standard) to track the locations of all archive samples. The historical archive from ISWS have been entered into this program as well.

14.2 Freezing of samples

The CAL is freezing all new archive samples as soon as they are processed at HM. This approach will improve the viability of the sample archive for NADP parameters and for emerging parameters or contaminants. Analyst will ensure sufficient headspace is available to minimize bottle integrity issues from liquid expansion during freezing.

14.3 Archive Preservation Study

It is believed that the former CAL at ISWS froze only the 3 long term sites, the 1 in 100 samples, and AMoN samples. It is not clear if they froze those samples as soon as processed or if they were frozen at the end of the year in which they were received. Although the CAL does not anticipate any detrimental effects to sample integrity from freezing all samples as soon as possible, due diligence will be taken to experimentally validate this. In addition, this study will determine if the sample integrity is maintained for 1-5 years of storage. To test this, the CAL set up a 5- year study with identical samples that are ***both frozen and refrigerated*** and ***tested annually*** to identify any changes in the analytes from either preservation method. All NTN analytes will be quantified in this study. The details of this study is outlined in **Appendix J**.

14.4 AMoN Current Sample Archive

Excess AMoN extracts will be frozen in the original extraction tubes. CAL will utilize a 2-year AMoN extract retention period. If samples remain 3 months past the 3rd year anniversary they will be discarded.

14.5 NTN Current Sample Archive

The Wisconsin arboretum site (WI06) has been added to the previous 3 “Forever” sites (NH02, NE15, IL11) The four “forever” sites (NH02, NE15, IL11 and WI06 (started in 2019) will have all available samples archived (frozen) for as long as each site is operational.

The previous ISWS 1 in 100 sample retention policy was replaced with a plan that represents 5 geographic regions as outlined below. Within each region there are 2 representative “fixed” sites from which a single monthly from each site samples will be archived (frozen) indefinitely. The CAL will try to save the first sample received each month from each site. If all samples are dry for a month there will not be a fixed archive for that month.

The 10 fixed sites are: CA99, CO99, FL11, NC41, NY20, OR97, TN11, TX16, WV18, and WY00 (See **Appendix J** for Archive Sites Summary Table and Maps).

The CAL plans to continue the 5-year NTN retention policy until a committee studies the issue. This

takes considerable storage space and the cost effectiveness of this policy needs to be evaluated. Currently, the full 6th calendar year archive will be offered to the community on/near the 6-year anniversary. The CAL will send out notification of the sample availability and post it on the NADP website. Samples remaining 3 months past the 6 year anniversary will be discarded. See **Appendix J** for table outlining the disposal schedule.

14.6 MDN Sample Archive

MDN samples are not archived.

14.7 Special Studies

The CAL can provide in-coming (current) and/or archived (already processed and frozen) samples upon request from the National Trends Network (NTN), and Ammonia Monitoring Network (AMoN). It is possible that the HAL could also entertain special study requests although there is not an archive sample available. Requests are evaluated by the PO, the Systems QA Manager and CAL managers for feasibility, scientific validity/support, and appropriate use of NADP samples.

The "Fixed" and "Forever" sites will only be approved for research of very significant magnitude after additional review by NOS and sign-off by the NADP Executive Committee.

There is a detailed guide explaining the approval process for special studies: "Guide for New Sample Archive Requests". Sample types, currently available for special studies are described below. Requestors will be invoiced a one-time set up fee and a per-sample fee plus shipping. If a request falls outside of the list below, the request will be evaluated and may be subject to other fees/potential denial.

<u>"Current" Samples (prior to archive)</u>

1. **Unfiltered Sample** – Up to ~850 mL of NTN sample, available upon receipt of samples at CAL.
2. **Sample Filter** – All NTN samples (except WI and WD) are filtered through a 0.45 µm Gelman® polyethersulfone 47mm filter. These filters can be placed into a labeled petri dish and made available for researchers upon receipt of samples at CAL if prior arrangements have been made. NOTE: This option applies only to the standard sample filtration volume of ~120 mL. If the entire sample (or a smaller filtration volume) is to be filtered, prior arrangements need to be made, and an extra charge will be applied.
3. **Filtered Sample** – Up to ~250 mL of filtered NTN sample, available upon receipt of samples at CAL. Additional volume could be filtered with possible extra cost.

<u>Archive Samples (samples already processed and frozen)</u>

1. **NTN Archive Sample** – up to ~60 mL of filtered sample is frozen for 5 years. These samples can be requested as follows:
    - **Active Archive Sample (up to 5 years post-collection):** up to ~30 mL is available beginning six months post collection.
    - **Expired Archive Sample:** up to ~60 mL is available after 5 years and are discarded after 6 years.
2. **AIRMoN Archive Sample** – up to ~60 mL of sample is frozen for two years. Up to ~30 mL is available six months post collection. **NOTE:** AIRMoN samples will not be available after 2021 due to the cessation of the AIRMoN network in September 2019.
3. **AMoN Extracts** – up to ~5 mL of each archived frozen sample is available 6 months after analysis. These samples are discarded after 2 years.

15 Revision Tracking Table

Rev. #	Date	Changes Made	Revised by
1	4/13/2020	Incorporated HAL and MDN throughout Removed AIRMoN from most sections Updated Organization language and charts Removed Labwide Policy and Reference Guide and added the Employee Handbook Added electronic lab notebook information and new reagent/chemical tracking process Added new NTN sample volume criteria Added new WI/WD syringe filter and dilution protocols Removed bromide references Corrected FL NT criteria to 80-120% Updated Data review process Moved most tables and figures to Appendices Updated all Tables and Figures Added new MDLs for 2020 Clarified MDL process for NTN and AMoN Added acronym table	Camille Danielson and Mark Olson

16 Signatures

Written by: Camille Danielson — Date: 5/1/2019
Title: QA Manager
Unit: NADP

Revised By: Mark Olson/Camille Danielson — Date: 4/13/2020
Titles: HAL Lab Manager and QA Manager
Unit: NADP

Approved by: Chris Worley — Date: 4/20/2020
Title: CAL Lab Manager
Unit: NADP

Approved by: Amy Mager — Date: 4/20/2020
Title: Sample and Data Processing Manager
Unit: NADP

Approved by: Martin Shafer — Date: 06/06/2020
Title: Systems QA and Special Projects Manager
Unit: NADP

Approved by: QAAG — Date: 6/24/2020
Title: Quality Assurance Advisory Group — Via Online survey

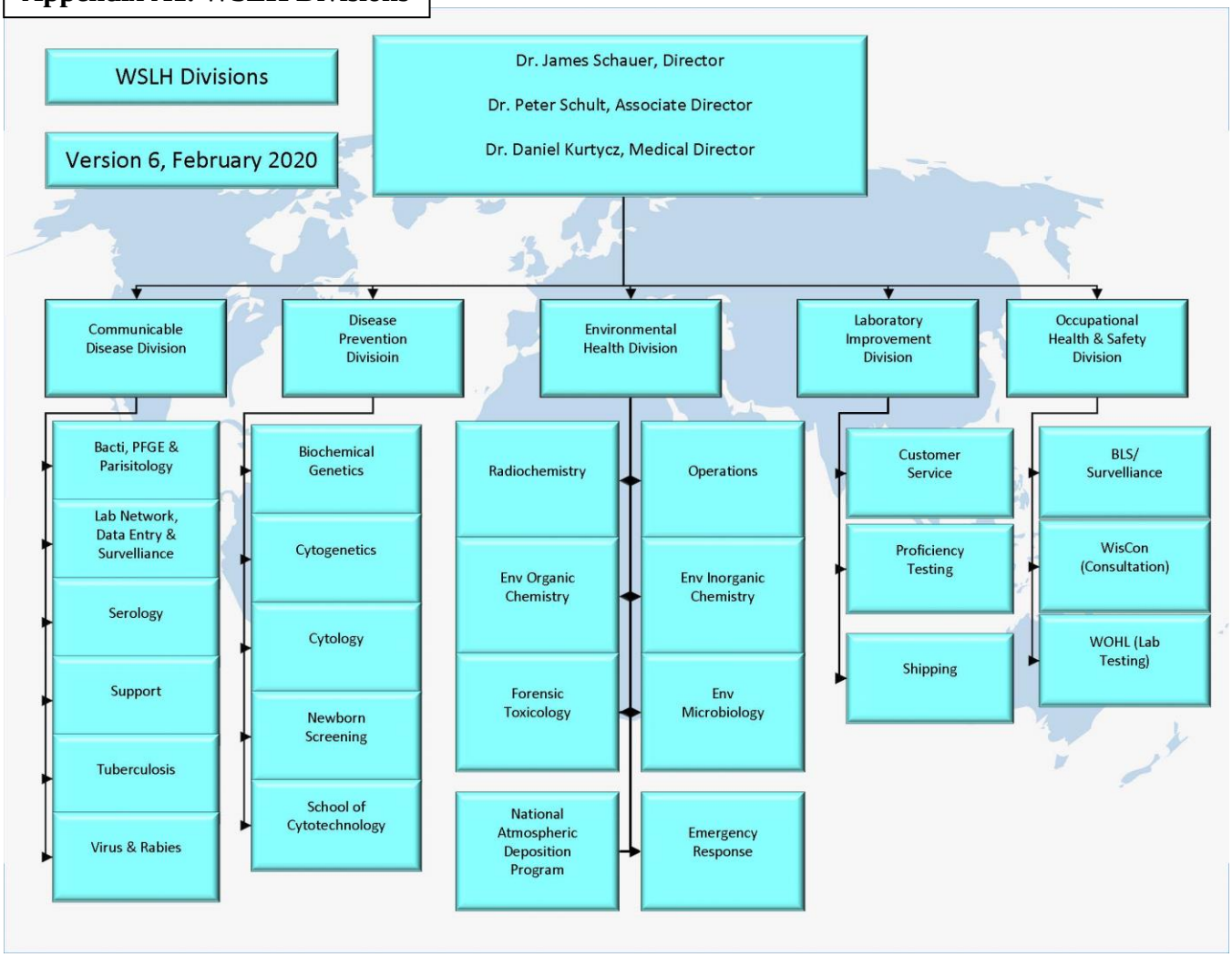
Unit: NADP

Approved by: David Gay — Date: 6/25/2020
Title: Program Office Coordinator
Unit: NADP

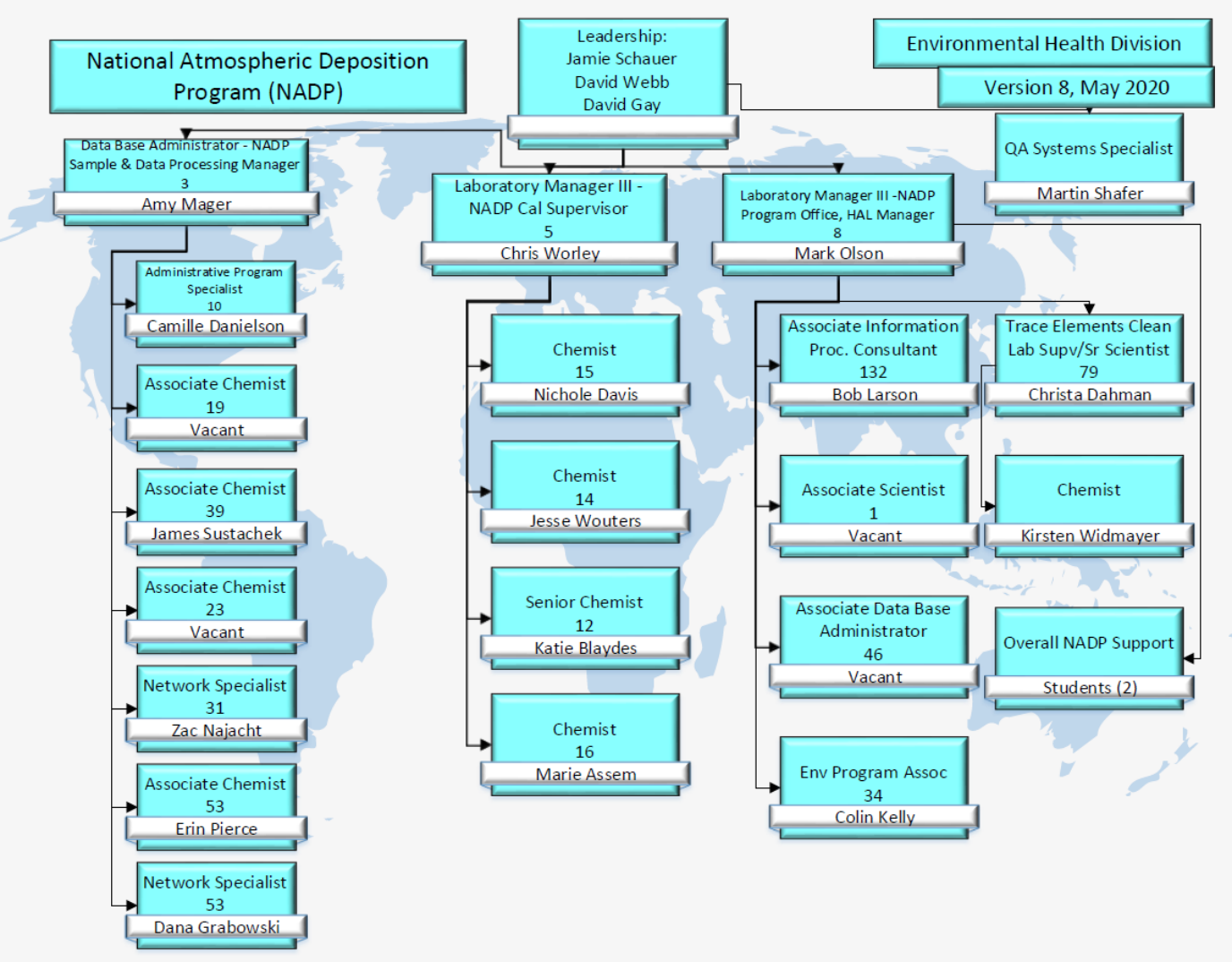
17 NADP CAL/HAL QAP Appendices

Appendix A WSLH Organizational Charts

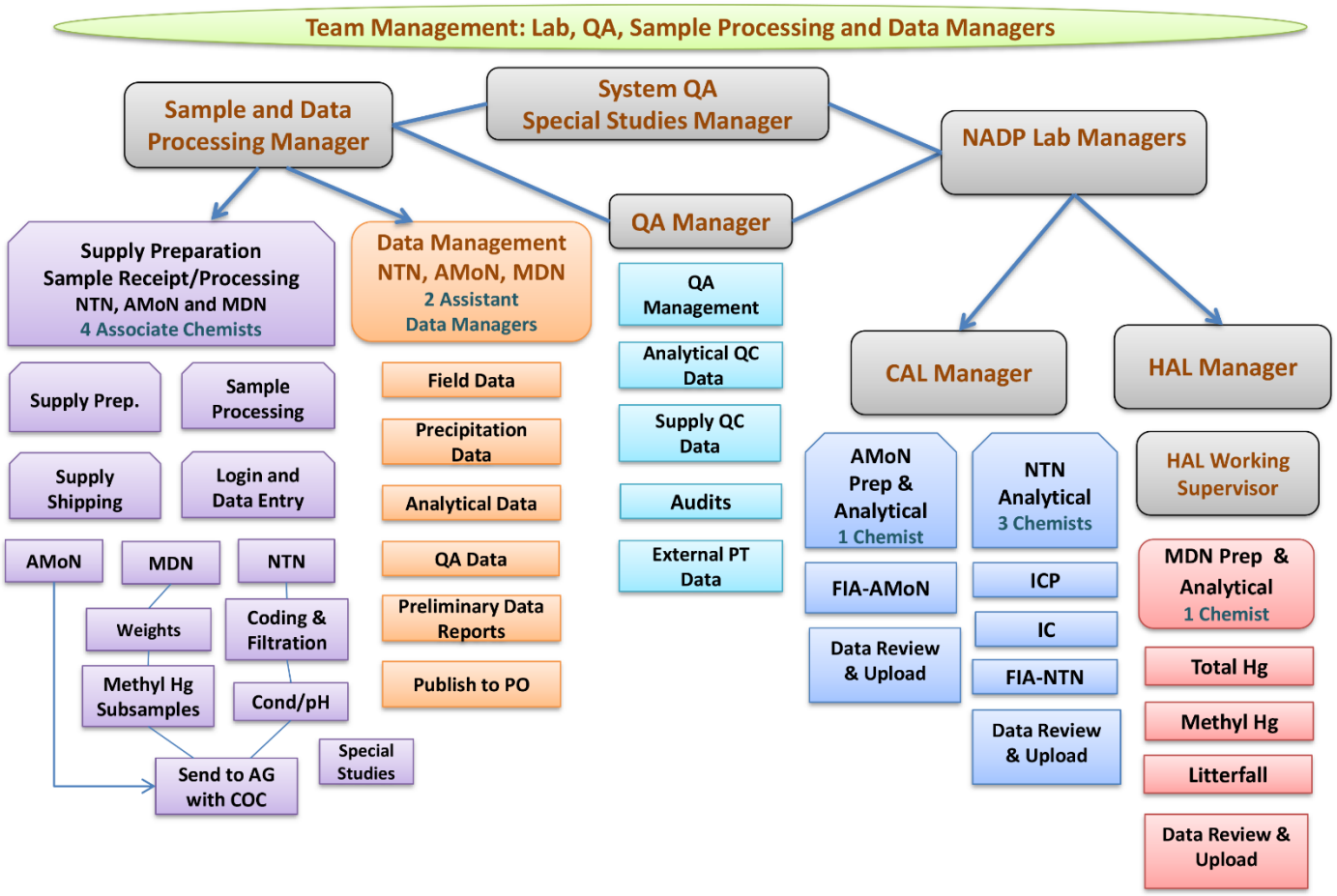
Appendix A1. WSLH Divisions



Appendix A2. EHD – NADP Organizational Chart (current 5/2020)



Appendix A3. NADP Laboratory Organizational Chart



Revision 2/26/2020

Appendix B Training

Appendix B1. Annual Training

EHD NADP Department
Annual DOC and Document Review Sign Off:

Form Revision 01/01/2020

*Signature and initials must be handwritten in ink. Completion dates will be used in the date column.

NAME: _____ **YEAR:** _____
SIGNATURE: _____ **INITIALS:** _____

DEMONSTRATION OF CAPABILITY (DOC) if applicable:

1. Analytical Method(s) Completion
   a. METHOD:_____ IDOC:__DOC:__ Run ID:_____ DATE:_____ INITIALS:_____
   b. METHOD:_____ IDOC:__DOC:__ Run ID:_____ DATE:_____ INITIALS:_____
   c. METHOD:_____ IDOC:__DOC:__ Run ID:_____ DATE:_____ INITIALS:_____
   d. METHOD:_____ IDOC:__DOC:__ Run ID:_____ DATE:_____ INITIALS:_____

GENERAL INFORMATION- SIGNOFF SHEET- REVIEW ANNUALLY

1. SAFETY CHECKLIST (either AG/HM or both) DATE:_____ INITIALS:_____
   http://slhicmsprod/regulatory-compliance/safety-topics/policies-procedures-and-plans/
   At link scroll down to employee checklist for your work area (AG or HM).

2. CHEMICAL HYGIENE PLAN (AG or HM) DATE:_____ INITIALS:_____
   O:\SOP\Safety\Final\AD_SAFETY_GENOP_102_Chemical Hygiene Plan.doc
   O:\SOP\Safety\Final\HM_SAFETY_GENOP_202_Chemical Hygiene Plan.doc

3. DATA INTEGRITY POLICY DATE:_____ INITIALS:_____
   O:\SOP\EHD\Division Wide\Final\EHD GENOP 029 SOP Data Integrity Procedure.doc

4. NADP CAL QA Plan REVISION #: _____ DATE:_____ INITIALS:_____
   O:\Teams\NADP\NADP Lab\SOPs\NADP FINAL SOPs\NADP CAL Quality Assurance Plan.pdf

5. EMERGENCY ACTION PLAN (either AG/HM) DATE:_____ INITIALS:_____
   O:\SOP\Safety\Final\AD_SAFETY_GENOP_101_Emergency Action Plan.doc
   O:\SOP\Safety\Final\HM_SAFETY_GENOP_201_Emergency Response Plan.doc

6. HIPAA REFRESHER DATE: INITIALS:
   https://compliance.wisc.edu/hipaa/training/

7. DISABILITY/ACCOMODATION TRAINING DATE:_____ INITIALS:_____
   (administered by HR)

8. OCCURENCE REPORTING PROCEDURE DATE:_____ INITIALS:_____
   O:\SOP\Labwide SOP Policies\Final\LABWIDE_GENOP_706_Occurence_Reporting_Procedure.doc

9. OCCURRENCE SYSTEM MANAGEMENT POLICY DATE:_____ INITIALS:_____
   O:\SOP\Labwide SOP Policies\Final\LABWIDE_GENOP_707_Occurence_System_Management_Policy.doc

11. LABWIDE ACCIDENT REPORTING DATE:_____INITIALS:_____
    O:\SOP\Safety\Final\LABWIDE_SAFETY_GENOP_301_ACCIDENT_REPORTING

RDA – 5 YRS

Page 1 of 1

Appendix B2. New Employee Training

New NADP Employee Training Documents

1. Safety

    1.1. Ag Drive and/or Henry Mall Safety **DATE**_____ **INITIALS**_____

        1.1.1. *http://slhicmsprod/faqs/employee-safety-checklists/*

    1.2. Emergency Response Plans **DATE**_____ **INITIALS**_____

        1.2.1. *http://slhicmsprod/faqs/emergency-response-plans/*

    1.3. Labwide Accident Reporting **DATE**_____ **INITIALS**_____

        1.3.1. *O:\SOP\Safety\Final\LABWIDE_SAFETY_GENOP_301_ACCIDENT_REPORTING*

2. Lab-wide Documents

    2.1. Chemical Hygiene Plan **DATE**_____ **INITIALS**_____

        2.1.1. *O:\SOP\Safety\Final\AD_SAFETY_GENOP_102_ Chemical Hygiene Plan.doc*

    2.2. Data Integrity Policy **DATE**_____ **INITIALS**_____

        2.2.1. *O:\SOP\EHD\Division Wide\Final\EHD GENOP 029 SOP Data Integrity Procedure.doc*

    2.3. EHD NELAC General chapter **DATE**_____
    INITIALS_____

        2.3.1. *O:\SOP\EHD\Division Wide\Final\NELAC QA Manual rev 16 2018\NELAC QA Manual rev 16 2018 1 General Chapter*

    2.4. Lab wide Policies Guide **DATE**_____
    INITIALS_____

        2.4.1. *O:\SOP\Labwide SOP Policies\Final\LABWIDE_GENOP_001_WSLH_Policy_Ref_Guide_Rev_9_June_1_2018.pdf*

    2.5. New Employee Training Checklist **DATE**_____
    INITIALS_____

    2.6. *O:\Teams\NADP\New Employee Onboarding Checklist*

    2.7. Building Access Authorization **DATE**_____ **INITIALS**_____

2.7.1. *O:\SOP\Labwide SOP Policies\Final\LABWIDE_GENOP_1004_Building_Access_Authorization.doc*

2.8. Computer use policy **DATE**_____ **INITIALS**_____

2.8.1.*O:\SOP\Labwide SOP Policies\Final\LABWIDE_GENOP_201_Computer_Use_Policy.doc*

2.9. HIPAA training **DATE**_____
INITIALS_____

2.9.1. *https://compliance.wisc.edu/hipaa/training/*

2.10. NADP Quality Assurance Plan **DATE**_____ **INITIALS**_____

2.10.1. *O:\Teams\NADP\NADP Lab\SOPs\NADP FINAL SOPs\NADP Quality Assurance Plan.docx*

2.11.Lab-wide Policy & Reference Guide **DATE**_____ **INITIALS**_____

2.11.1. *O:\SOP\Labwide SOP Policies\Final\LABWIDE_GENOP_001_WSLH_Policy_Ref_Guide_Rev_9_June_1_2018.pdf*

2.12. Occurrence Reporting and Policies **DATE**_____ **INITIALS**_____

2.12.1. *O:\SOP\Labwide SOP Policies\Final\LABWIDE_GENOP_706_Occurence_Reporting_Procedure.doc*

2.12.2. *O:\SOP\Labwide SOP Policies\Final\LABWIDE_GENOP_707_Occurence_System_Management_Policy.doc*

2.13. Disability Accommodation Training **DATE**_____ **INITIALS**_____

2.13.1. *O:\Teams\NADP\Mandatory Disability Accommodation Training\Mandatory Disability Letter*

2.13.2. *O:\Teams\NADP\Mandatory Disability Accommodation Training\WSLH Disability Training 2019*

2.13.3. *O:\Teams\NADP\Mandatory Disability Accommodation Training\WSLH Disability Accommodation Training Quiz 2019*

3. Method Specific Training

3.1. Method Training Sign off Form **DATE**_____ **INITIALS**_____

3.1.1. *O:\Teams\NADP\NADP Lab\LAB Final Forms\Training\Method Training Form Version 1*

3.2. Initial Demonstration of Capability (IDOC) Form **DATE**_____ **INITIALS**_____

3.2.1. *O:\Teams\NADP\NADP Lab\LAB Final Forms\DOCs\NADP Initial Demonstration of Capability.docx*

Appendix C. NADP Equipment

Appendix C1. NADP Analytical Equipment

Analysis	Type	Species	Instrument
Inductively Couple Plasma – Optical Emission Spectrometer (ICP-OES)	Base Cations	Na^+, K^+, Ca^{2+}, Mg^{2+}	Agilent 5100
Ion Chromatography (IC)	Acid Anions	Cl^-, NO_3^-, SO_4^{2-}	3 Dionex Integrions
Flow Injection Analysis Precipitation Samples (FIA-NTN)	NH_4 and PO_4	NH_4^+ and PO_4^{3-}	Lachat Quik Chem 8500 S2
Flow Injection Analysis AMoN Extracts (FIA – AMoN)	NH_4	NH_4^+	Lachat Quik Chem 8500 S2
pH-Manual	pH Manual	H^+	Mettler S700
SpC- Manual	Specific Conductance Manual	Charged Species	Mettler S700
SpC-Automated	Specific Conductance Automated	Charged Species	SCP TitrEC
Cold Vapor Atomic Fluorescence Spectrometer	Total Mercury	Hg	Tekran 2600
Cold Vapor Atomic Fluorescence Spectrometer	Methyl Mercury	CH_3Hg^+	Tekran 2700
Atomic Absorption Spectrophotometer	Mercury in solids	Hg	Nippon MA3000

Appendix D. Detection Limits

Appendix D1. NTN Method Detection Limits

Analyte	2018 Lab MDL_L	2019 Lab MDL_L	2020 Lab MDL_L	2018 Network MDL_N	2019 Network MDL_N	2020 Network MDL_N
Ca	0.004	0.001	**0.008**	0.011	0.023	**0.023**
Mg	0.002	0.001	**0.001**	0.003	0.006	**0.006**
Na	0.003	0.002	**0.001**	0.004	0.010	**0.010**
K	0.002	0.003	**0.002**	0.005	0.005	**0.005**
Cl	0.006	0.004	**0.003**	0.006	0.018	**0.018**
SO_4	0.008	0.007	**0.005**	0.007	0.018	**0.018**
NO_3	0.003	0.003	**0.006**	0.008	0.018	**0.018**
Br	0.003	0.002	**NA**	0.006	0.006	**NA**
NH_4	0.004	0.002	**0.007**	0.008	0.017	**0.017**
PO_4	0.003	0.003	**0.004**	0.008	0.010	**0.010**
pH	0.01	0.01	**0.01**	0.01	0.01	**0.01**
Conductivity	0.9	0.9	**0.9**	0.9	0.9	**0.9**

Appendix D2. AMoN Detection Limits

AMoN	2018 Lab MDL	2019 Lab MDL	**2020 Lab MDL**	2018 Network MDL	2019 Network MDL	**2020 Network MDL**
mg/L NH_4	0.008	0.016	**0.013**	0.119	0.104	**0.083**

Appendix D3. MDN Detection Limits

Analyte - Platform	Limit of Detection as Mass (pg)	Standard Sample Volume (mL)	Method Detection Limit (ng/L)	Limit of Quantitation (ng/L)
Total Hg - Tekran 2600	6	30	0.2	0.667
Methyl Mercury - Tekran 2700	3	30	0.1	0.333

Appendix D4. NTN Historical Network Detection Limits

NTN Historical Method Detection Limits (mg/L)

Sample Start ID	Sample End ID	Ca	Mg	Na	K	NO3	SO4	Cl	Br	NH4	PO4
NA1801	NA3361	0.020	0.002	0.004	0.004	0.030	0.010	0.050	NA	0.020	0.003
NA3362	NA3475	0.008	0.002	0.004	0.004	0.030	0.010	0.050	NA	0.020	0.003
NA3476	NA3695	0.008	0.002	0.002	0.002	0.030	0.010	0.050	NA	0.020	0.003
NA3696	NA4254	0.006	0.002	0.002	0.002	0.030	0.010	0.050	NA	0.020	0.003
NA4255	NA6000	0.008	0.002	0.002	0.002	0.030	0.010	0.050	NA	0.020	0.003
NA6001	NA6328	0.008	0.002	0.002	0.003	0.030	0.010	0.020	NA	0.010	0.003
NA6329	NA6543	0.024	0.009	0.002	0.003	0.030	0.010	0.020	NA	0.010	0.003
NA6544	NA6650	0.009	0.002	0.002	0.003	0.030	0.010	0.020	NA	0.010	0.003
NA6651	NA7299	0.009	0.002	0.002	0.003	0.030	0.010	0.020	NA	0.020	0.003
NA7300	NA7741	0.009	0.003	0.002	0.003	0.030	0.010	0.020	NA	0.020	0.003
NA7742	ND1937	0.009	0.003	0.003	0.003	0.030	0.010	0.020	NA	0.020	0.003
ND1938	ND1938	0.009	0.003	0.003	0.003	0.030	0.010	0.030	NA	0.020	0.003
ND1939	ND2633	0.009	0.003	0.003	0.003	0.030	0.030	0.030	NA	0.020	0.003
ND2634	NF4630	0.009	0.003	0.003	0.003	0.030	0.030	0.030	NA	0.020	0.010
NF4631	NH6700	0.009	0.003	0.003	0.003	0.030	0.030	0.030	NA	0.020	0.020
NH6701	NM6824	0.009	0.003	0.003	0.003	0.030	0.030	0.030	NA	0.020	0.020
NM6825	NS3700	0.009	0.003	0.003	0.003	0.030	0.030	0.030	NA	0.020	0.003
NS3701	NU7200	0.009	0.003	0.003	0.003	0.010	0.010	0.005	NA	0.020	0.003
NU7201	NW0218	0.009	0.003	0.003	0.003	0.010	0.010	0.005	NA	0.020	0.009
NW0219	NZ9957	0.009	0.003	0.003	0.003	0.010	0.010	0.005	NA	0.020	0.006
NZ9958	TA0214	0.009	0.003	0.003	0.003	0.009	0.013	0.008	NA	0.020	0.006
TA0215	TA0334	0.002	0.001	0.003	0.001	0.009	0.013	0.008	NA	0.020	0.006
TA0335	TB4169	0.002	0.001	0.003	0.001	0.009	0.013	0.008	NA	0.005	0.006
TB4170	TE3724	0.002	0.001	0.001	0.001	0.017	0.010	0.003	NA	0.004	0.004
TE3725	TG9571	0.006	0.001	0.001	0.001	0.009	0.010	0.004	NA	0.006	0.004
TG9572	TI2460	0.004	0.001	0.003	0.001	0.005	0.004	0.003	NA	0.010	0.008
TJ5599	TM2704	0.005	0.002	0.002	0.003	0.010	0.010	0.009	0.005	0.009	0.005
TM2705	TN2615	0.019	0.005	0.005	0.001	0.007	0.005	0.008	0.005	0.017	0.009
TN2616	TP0369	0.009	0.002	0.006	0.002	0.005	0.005	0.005	0.005	0.016	0.005
TP0370	TQ4360	0.009	0.002	0.003	0.004	0.005	0.004	0.005	0.004	0.019	0.005
TQ4361	TS9999	0.006	0.002	0.002	0.002	0.005	0.005	0.003	0.004	0.018	0.006
TT0001	TT7317	0.011	0.003	0.004	0.005	0.008	0.007	0.006	0.006	0.008	0.008
TT7318	TV0257	0.023	0.006	0.010	0.005	0.018	0.018	0.018	0.006	0.017	0.010
TV0258	Ongoing	0.023	0.006	0.010	0.005	0.018	0.018	0.018	0.006	0.017	0.010

Appendix E. Supply QC

Appendix E1. Supply Lot Approval QC Log In and frequency for NTN and MDN

NADP Supply Lot Approval QC Frequency and Log In (Revision 6/23/2020)

Item	Solution	Amount & Frequency	Project LOG IN	Client Number	LIMS Description
BAG LOTS					
NTN Sample Bags	~150 mL MQ	20/new lot (unless <500 then 10)	**New Sampling Bag Lot Check**	Date Prepared and Preparer Initials	Bag Type, Lot #, Bag# (i.e. NTN Sample Bag Lot 32344 1 of 20)
NTN Bucket Bags	~150 mL MQ	5/new lot	**Bag Blank Study**	Date Prepared and Preparer Initials	Bag Type, Lot #, Bag# (i.e. NTN Bucket Bag Lot 32344 1 of 5)
NTN LID Bags	~150 mL MQ	5/new lot	**Bag Blank Study**	Date Prepared and Preparer Initials	Bag Type, Lot #, Bag# (i.e. NTN lid bag Lot 32344 1 of 5)
BOTTLE LOTS					
NTN 60mL HDPE Bottles	~60mL MQ	10/new lot (unless <100 in lot then 5)	**NADP New Bottle Blanks**	Date Prepared and Preparer Initials	Bottle Type, Lot #, Bottle# (i.e. 60mL NTN Lot23238 1 of 10)
NTN 1 Liter HDPE (New)	~150 mL MQ	10/new lot (unless <100 in lot then 5)	**NADP New Bottle Blanks**	Date Prepared and Preparer Initials	Bottle Type, Lot #, Bottle# (i.e. 1L NTN Lot44348 1 of 10)
MDN 250 mL, 1L or 2L PETG	20 mL 1% HCl + 100mL	10/new lot (unless <200 in lot then 5)	**MDN Bottle Blanks**	Date Prepared and Preparer Initials	Bottle Type, Lot #, BottleID, Bottle# (i.e. 250mL MDN Lot 126 Bottle 1 of 10)
FILTER LOTS					
NTN 47mm Disc Filters	60 mL MQ	20/New Lot min 2 boxes from lot	**Filter Blank Lot Testing**	Date Prepared and Preparer Initials	Lot, Box#, Filter #, Brand and filter type
NTN Syringe Filters	20 mL MQ	5 per lot of 150 or less	**Filter Blank Lot Testing**	Date Prepared and Preparer Initials	Lot, Box#, Filter #, Brand and filter type
TUBE LOTS					
NTN Test Tubes	2-10 mL MQ	10/New Lot ICP/FIA	**Test Tube QC Blank**	Date Prepared and Preparer Initials	Brand, Test tube type, lot # and tube # (i.e. Fisher, ICP, Lot 3434, 2 of 10)
OTHER LOTS					
MDN Acid Preservative	30 mL	1/Batch of Acid Preservative	**Acid Checks**	Date Prepared and Preparer Initials	"Acid Preservative Blank", Acid Lot # and Batch ID
Must Meet LOT Approval Before Use of these Supplies					

Appendix E2. Ongoing Supply QC Log In and frequency for NTN and MDN

NADP Ongoing Supply QC Frequency/Log In (Revision 6/24/2020)

Item	Project Log In	Client Number	LIMS Description	Solution	Amount/Frequency
TYPE I WATER					
MDN Type 1 Water	MQ Water System Blanks	Date Prepared & Initials	"Hg Type 1 Water Blank", BLDG, Lab # (i.e. Type 1 Blank, AG 200, HM135)	100 mL MQ	1/purifier/week
NTN Type 1 H_2O Blanks	MQ Water System Blanks	Date Prepared & Initials	"Type 1 Water Blank", BLDG, Lab # (i.e. Type 1 Blank, AG 200B, HM135)	60 mL MQ	1/purifier/week
ONGOING Supply Tests NTN					
NTN 47mm Disc Filters	Filter Blanks DI	Date Prepared & Initials	"Start/End Filter" and Sample Range	60 mL MQ	2/ Filter Day
NTN Syringe Filters	Weekly Syringe Filter Blank	Date Prepared & Initials	"Syringe Filter Blank", Syringe and Filter Lot#	20 mL MQ	1 per week
NTN Sample Bags	Bag Blank Study	Date Prepared & Initials	Bag Type, Lot#	~150 mL MQ	1/week
NTN 1 Liter HDPE	Bottle Blanks	Date Prepared & Initials	"1L NTN Washed"	~150 mL MQ	1/wash day
NTN Buckets	Bucket Blanks	Date Prepared & Initials	"New" or "Used" "Bucket"	~150 mL MQ	1/wash day
NTN LIDS	Lid Blanks	Date Prepared & Initials	Lid Type	~100 mL MQ	1/wash day /per type
ONGOING Supply Tests MDN					
MDN Sample Train	Sample Train Blanks	Date Prepared & Initials	"Sample Train Preparation Week"	~ 100 mL MQ	1/week in bag for ≥2 days
MDN Acid Bath	Acid Checks	Date Prepared & Initials	"Acid Bath Blank", BathID	10 mL	1/Acid Bath/month
USGS System Blanks	USGS System Blanks	Date Logged & Initials	USGS ID for blanks, Blank 1 of 2	Hi purity H_2O	2/Quarter
PTs					
NTN WMO PTs	WMO/GAW	WMO Sample ID	"WMO PT X of X"	As Sent	2/year
NTN ECCC PTs	ECCC PT Samples	ECCC Sample ID	"ECCC NTN PT X of X"	As Sent	2/year
NTN USGS PTs	USGS Intercomparison	USGS Sample ID	"USGS NTN PT X of X"	As Sent	Monthly
MDN USGS PTs	MDN PT Samples	USGS Sample ID	"USGS MDN PT X of X"	As Sent	Monthly
MDN ECCC PTs	ECCC PT Samples	ECCC Sample ID	"ECCC MDN PT X of X"	As Sent	Annual
QC STANDARDS					
NTN MDL Sample	NTN MDL Sample	Date Prepared & Initials	NADP MDL Solution ID, Bag Lot if new	200 mL MDL solution	As needed
Test QC Standards	QA New Standard Check	FMDL# (i.e. FMDL2003), Initials	NADP Solution# (for testing of new FMDL or new FR50 or other QCS)	Varies	As needed
Official QC Standard	Lab QC	FXXXXXXX (8 digits req), initials	NADP Solution# (for any standard with limits set in LIMS)	Varies	As needed
Special Checks	Special QA Checks	Date Prepared & Initials	Information on what is being tested	Varies	As needed

Appendix E3. Supply QC Log In and frequency for AMoN

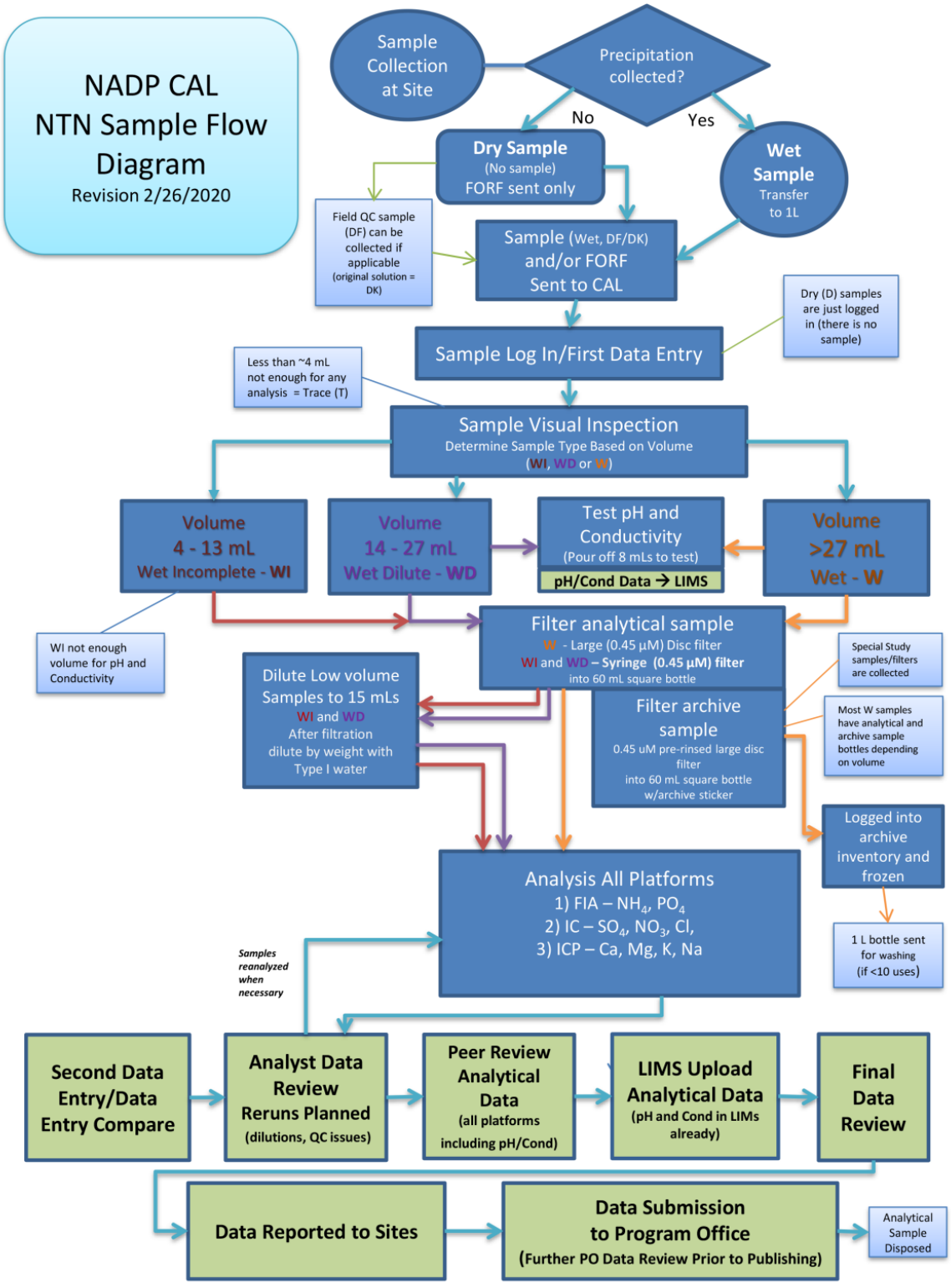
Item	Solution	Amount & Frequency	Project LOG IN	Client Number	LIMS Description
Jars					
Glass Jar – NEW	10 mL MQ	1/wash batch	**AMoN QA Samples**	Date Washed	**GJ New, Batch letter and Lot # if available**
Glass Jar – USED	10 mL MQ	1/wash batch	**AMoN QA Samples**	Date Washed	**GJ Used, batch letter**
Blanks With Cores					
Core Blanks	10 mL MQ	1/sampler assembly day per lot used; 2/lot if new lot	**AMoN QA Samples**	Date Extracted	**Core Blank, Sampler batch IDs and Core lot**
Prep Blanks (body+core+jar)	10 mL MQ	1/sampler prep batch	**AMoN QA Samples**	Date Extracted	**Preparation Blank, Samper batch ID and Core lot**
Water Only Blanks					
Sonicator Blank	10 mL Sonicator H2O	1/sampler prep batch at end of prep	**AMoN QA Samples**	Date Prepped	**Sonicator Blank, Sampler batch**
Method Blank (extraction water)	10 mL MQ	1/extraction day	**AMoN QA Samples**	Date Prepped	**Method Blank, water source**
Water Blank (MQ used in sonicator)	10 mL MQ from MQ system	1/2nd preparation day	**AMoN QA Samples**	Date Prepped	**Water Blank, water source**
Hood/Room Blanks					
2 Week Blank Sonicator Hood	10 mL MQ	1/two week period	**AMoN QA Samples**	Date Extracted	**AIR Sonic Hood 2 wk, Deployment Minutes**
2 Week Blank Extraction Hood	10 mL MQ	1/two week period	**AMoN QA Samples**	Date Extracted	**AIR Extraction Hood 2 wk, Deployment minutes**
Extraction Day ONLY Blank	10 mL MQ	1 per extraction day	**AMoN QA Samples**	Date Extracted	**Extraction Hood Blank, Deployment Minutes**
2 Week Room Blank	10 mL MQ	1/two week period	**AMoN QA Samples**	Date Extracted	**Room Blank, Deployment Minutes**

Appendix E4. AMoN Preparation QC Criteria

NADP CAL AMoN Preparation QC (Revision 2/28/2020)

QC Type	Description	Frequency	Criteria	Origin of Criteria	Corrective Action
Preparation Blank	Fully Assembled core, body, coupler placed in jar/bag, frozen overnight before extraction	1 per sampler preparation batch (each sonicator batch is 1 batch)	<0.044 mg/L NH_4	Less than median travel blank level 2018	Determine if the whole batch or a core lot issue. If possible re-clean samplers in batch and/or replace cores and retest. Or add qualifier to samplers (h flag = QR B).
Core Blank	Brand new core extracted along with other QC	1/sampler assembly day/previous lot 2/sampler assembly day/new lot	<0.044 mg/L NH_4	Less than median travel blank level 2018	Assess scope of issue/number of cores high. Action can include: test 2-3 more cores from lot, reassemble cleaned samplers with new cores/retest, return core lot, prepare entire batch of samplers, qualify data from batch of samplers (h flag = QR B).
Jar Blank	Cleaned new or used jar + 10 mL Type I, turned upside down, left overnight, and analyzed	1 per wash batch	<0.016 mg/L NH_4	Less than median travel blank level 2018	Pull additional jar(s) from wash batch if possible. Look at related core/prep blanks for root cause. Check cleaning including: bins, bin liner, dishwasher, jar caps.
Method Blank	Type I water from the auto dispenser used to do extractions	1 per extraction day	<0.022 mg/L NH_4	1/2 Prep blank criteria	Compare to samplers/QC from same extraction. If possible take another sample from dispensing jar. Samples associated with blank must be qualified due to possible contamination (h flag = QR of B).
Sonicator Blank	Water from the sonicator after last step in the cleaning process	1 per preparation day per sonicator	<0.016 mg/L NH_4	Analytical NH_4 MDL_L	Use with other QC samples to determine root cause. Indicates potential issue with cleaning. Action includes: cleaning of the sonicator baths, racks and covers, test Type I water, check source of cleaning solutions.
Water Blank	Sample of Type I water from MilliQ system used to fill sonicator/auto dispenser	1 per preparation day	<0.016 mg/L NH_4	Analytical NH_4 MDL_L	Repeat test of MilliQ system. If fails again have the system serviced and utilize another water source if possible. Review other QC samples from the same system (weekly MQ blanks) to assess longevity of the issue.
Hood Extraction Blank	Sampler hung in the hood during the extraction (deployment of 1-5 hours normally)	1 per extraction day	<0.2 mg/L NH_4	Travel Blank Criteria	Check filters and review QC from same extraction for correlation with higher blank values. Check for power failures or other issues with hoods.
Room Blank	Sampler deployed in the extraction room (not in a hood) for 2 week period	1 per two week period	<0.8 mg/L NH_4	2 X Hood Criteria	Room should be checked for possible sources of ammonia or ventilation issue.
Hood - 2 Week Blank	Sampler deployed in hoods for two week period	1 per two week period per hood	<0.4 mg/L NH_4	2 X the travel blank criteria	Review QC samples from same time period for a correlation with higher blank values if hood criteria is exceeded. Check for power failures or other issues (filters) with hoods.
Travel Blanks	Fully prepared sampler sent along with sampler to be deployed	25% of sites receive travel blanks each deployment in a rotating manner	<0.2 mg/L NH_4	Historical NADP TB Criteria (currently = 5 X median TB)	Check FORF for possible field issues (i.e. accidental deployment). High TB flagged with a t flag which does not affect QR. Samplers from same site (A, B, C) not flagged. Check Body IDs for length of use.
Duplicates	2 samplers sent to site for deployment (may incorporate 1 newer sampler per duplicate batch to help identify body age issue)	15% of sites receive duplicates each deployment in a rotating manner	15% RPD for results over 10 X MDL_N	Above reasonably expected variation	Duplicate results over 10 X MDL > 15% RPD should be reanalyzed. Body IDs checked for age/# of uses as possible cause (permeability/cleanliness). Both sampler results flagged (h flag = QR of B).

Appendix F1. NTN Sample Flow



Appendix G. Sample Notes Codes for Networks

Appendix G1. NTN Sample Notes Codes

NTN Sample Condition Flags		
Notes	**Description**	**QR Code[1]**
a	Incomplete laboratory analysis	B
b	Bulk sample	C
c	Grossly contaminated sample	C
d	Visible debris in sample	B
e	Extended sampling period (>194 hrs.)	C
f	Major field protocol issue	C
h	Sample handling issue (handling contamination in the field or leakage upon receipt in the lab)	B
i	Low volume (diluted) sample	B
l	Laboratory error	C
m	Missing data	B
n	No sample deployed	---
p	Precipitation value unknown	C
u	Undefined sample	C
v	Precipitation amount indicates sufficient sample for analysis, but insufficient sample in bottle.	C
z	Site operation issue	B

[1]Quality Rating (QR) Code Definitions: A – Fully qualified data;
B Valid data with minor issues; C – Invalid data

Appendix G2. AMoN Sample Notes Codes

AMoN Sample Condition Flags		
Notes	**Description**	**QR Code[1]**
a	Laboratory analytical data missing	C
c	Local source of ammonia (within ~500m), based on site operator comments	B
d	For T samples "d" indicates < lab method detection limit (mg/L NH_4) For A, B and C samples "d" indicates < network method detection limit (mg/L NH_4)	B
e	Long sample time (> 360 hours)	B
f	Major field sampling issue (gross contamination, vandalism, etc.)	C
h	Sample handling issue in field, shipping, or laboratory	B
l	Major laboratory issue	C
m	Missing data from field operator	B
n	No sampler deployed	C
s	Short sample time (< 312 hours)	No change
t	Elevated travel blank concentration (>0.2 mg/L NH_4). Elevated travel blank concentration should be considered when utilizing the associated ambient sampler data.	B
y	Delayed sample processing (>21 days from date off to analysis date)	B

[1] Quality Rating (QR) Code Definitions:
A – Fully qualified data
B – Valid data with minor issues
C – Invalid data

Appendix G3. MDN Sample Notes Codes

MDN Sample Condition Notes Codes		
Notes	**Description**	**QR Code[1]**
b	Bulk sample (sample exposed the whole time)	C
c	Contaminated sample	C
d	Visible debris in sample	B
e	Extended sampling period (> 194 hrs.)	B
f	Field protocol error (serious problems in field operations that compromise sample integrity)	C
h	Sample handling issue (handling contamination in the field, significant leakage upon receipt in the lab, rec'd date 16-30 days after OFF date)	B
i	Low volume sample (sample volume < 10ml)	B
l	Laboratory error	C
m	Missing data	B
n	No sample submitted (no sample or sample receipt > 30 days after OFF date)	C
p	Precipitation value unknown (no precipitation data from rain gage or alternate source)	C
u	Undefined sample (sample exposed for at least 6 hours without precipitation)	C
q	Minor quality control issue	B
v	Precipitation amount indicates sufficient sample for analysis, but insufficient sample in bottle. (undercatch; sample volume < 1.5ml or sample volume is < 10% of rain gage precipitation amount)	C
z	Site operation issue (min temp < 32, max temp > 120 deg F)	B

[1]Quality Rating (QR) Code Definitions:
A – Fully qualified data
B – Valid data with minor issues
C – Invalid data

NADP Sample Criteria for Field, Shipping & Handling Conditions

Network	Condition	Criteria	Notes/SL Code	QR Code (validity)
Field Issues				
NTN	Extended sampling period	Difference between ON/OFF date >194 hrs.	"e" - extended time	C
MDN	Extended sampling period	Difference between ON/OFF date >194 hrs.	"e" - extended time	B
AMoN	Short sampling time	Sampler deployed for < 312 hrs.	"s" - short sample time	no change
AMoN	Long sampling time	Sampler deployed for > 360 hrs.	"e" - extended time	B
Handling/Shipping Issues				
NTN	Sample late from site (16)	Received date > 16 days after OFF date	"h" - sample handling	B
NTN	Very late sample (60)	Received date > 60 days after OFF date	"F" - SL code for major field protocol issue	C
MDN	Sample late from site (16)	Received date > 16 days after OFF date	"h" - sample handling	B
MDN	Sample late from site (30)	Received date > 30 days after OFF date	"n" - no sample; very late	C
MDN	Very late sample (60)	Received date > 60 days after OFF date	"n" - no sample; very late	C
AMoN	Major field sampling issue	gross contamination, vandalism, field protocol	"f" - major field issue	C
Analysis/Lab Time Related Issues				
NTN	Late lab analysis	Lab date > 60 days after Received date	"h" - sample handling	B
NTN	Laboratory error	Major laboratory error	"L" - SL code for major laboratory issue	C
MDN	Late lab analysis	Lab date > 60 days after Received date	"h" - sample handling	B
MDN	Late sample preservation	> 60 days between Received date & Preservation date	reviewer error flags only	no change
AMoN	Delayed sample processing	Analysis Date > 16 days after OFF date	"y" - delayed analysis	B
AMoN	Sample handling issue	sample handling issue in field, shipping or lab	"h" - sample handling	B
AMoN	Major lab issue	major sample handling issue in lab	"l" - major lab issue	C

Appendix H. Example Run Protocol

Appendix H1. IC Partial Run Template

Example IC run template				
Solution Label	QCS & Target Values	Cl	SO4	NO3
RINSE	MDL	0.018	0.018	0.018
RINSE	FR502001	0.104	0.958	0.898
S1	FL190001	0.025	0.025	0.025
S2	FMDL2001	0.050	0.078	0.031
S3	FCRM2003	0.359	0.610	0.184
S4	FM180003	0.500	0.500	0.500
S5				
S6				
S7				
S8				
FB190001	±MDL			
FR502001	90-110%			
FL190001	80-120%			
FMDL2001	±MDL			
FCRM2003	85-115%			
SAMPLE 1				
SAMPLE 2				
SAMPLE 3				
SAMPLE 4				
SAMPLE 5				
SAMPLE 6				
SAMPLE 7				
SAMPLE 8				
SAMPLE 9				
SAMPLE 10				
SAMPLE 2-Q	DUP*			
FM180003	90-110%			
FB190001	±MDL			
SAMPLE 11				
SAMPLE 12				
SAMPLE 13				
SAMPLE 14				
SAMPLE 15				
SAMPLE 16				
SAMPLE 17				
SAMPLE 18				
SAMPLE 19				
SAMPLE 20				
SAMPLE 16-Q	DUP*			
FM180003	90-110%			
FB190001	±MDL			

Appendix I. QC Standards Tables

Appendix I1. CAL Control Limits

NADP Combined Control Limits					
Revision: 19	3/11/2020				
ID	Criteria	Ca	K	Mg	Na
FB190001	±MDL	0.023 (-0.023-0.023)	0.005 (-0.005-0.005)	0.006 (-0.006-0.006)	0.01 (-0.01-0.01)
FR50190#	±MDL	0.13 (0.107- 0.153)	0.022 (0.017-0.027)	0.023 (0.017-0.029)	0.057 (0.047-0.067)
FLP18001	90-110%	2.5 (2.25-2.75)	2.5 (2.25-2.75)	2.5 (2.25-2.75)	2.5 (2.25-2.75)
FH180002	90-110%	5.0 (4.5-5.5)	5.0 (4.5-5.5)	5.0 (4.5-5.5)	5.0 (4.5-5.5)
FL190001	80-120%	0.05 (0.04 - 0.06)	0.05 (0.04 - 0.06)	0.05 (0.04 - 0.06)	0.05 (0.04 - 0.06)
FM180002	90-110%	0.5 (0.45-0.55)	0.5 (0.45-0.55)	0.5 (0.45-0.55)	0.5 (0.45-0.55)
ID	Criteria	NH_4 (NTN/AIRMON)	OPO_4		
FB190001	±MDL	0.017 (-0.017-0.017)	0.01 (-0.01-0.01)		
FR50190#	90-110%	0.250 (0.225-0.275)	NA		
FL190001	80-120%	0.05 (0.04 - 0.06)	0.015 (0.012-0.018)		
FM190002	90-110%	0.600 (0.660-0.540)	0.200 (0.220-0.180)		
ID	Criteria	Cl	SO_4	NO_3	
FB190001	±MDL	0.018 (-0.018 - 0.018)	0.018 (-0.018 - 0.018)	0.018 (-0.018 - 0.018)	
FR50190#	90-110%	0.104 (0.094 - 0.114)	0.958 (0.862-1.054)	0.898 (0.808-0.988)	
FL190001	80-120%	0.025 (0.02-0.03)	0.025 (0.02-0.03)	0.025 (0.02-0.03)	
FM180003	90-110%	0.5 (0.45-0.55)	0.5 (0.45-0.55)	0.5 (0.45-0.55)	
ID	Criteria	NH_4 (AMoN)			
FB190001	±MDL	0.016 (-0.016- 0.016)			
FR50190#	90-110%	0.250 (0.225-0.275)			
FL190001	80-120%	0.05 (0.04 - 0.06)			
FMAM2001	90-110%	0.750 (0.675-0.825)			

QC ID	Description	
FB190001	Calibration Blank - Type 1 Water.	AMoN LDR= 10 mg/L; No Carryover up to 10 mg/L
FR50190X	Faux Rain Solution - ~50% NTN Concentration.	Lachat NH4 & OPO4 LDR= 10 mg/L; No Carryover up to 10 mg/L
FL190001	Quality control sample at low level - second source.	ICP LDR= Mg=10 mg/L, K,Ca, Na =20mg/L ; No carryover up to 10 mg/L
FM180002 or FM190002	Quality control sample at mid level - same source as curve.	IC LDR= 15 mg/L; No carryover up to 15 mg/L
FMAM2001	Quality control sample at mid level - for AMoN (NH_4 only no PO_4) - same source as curve.	

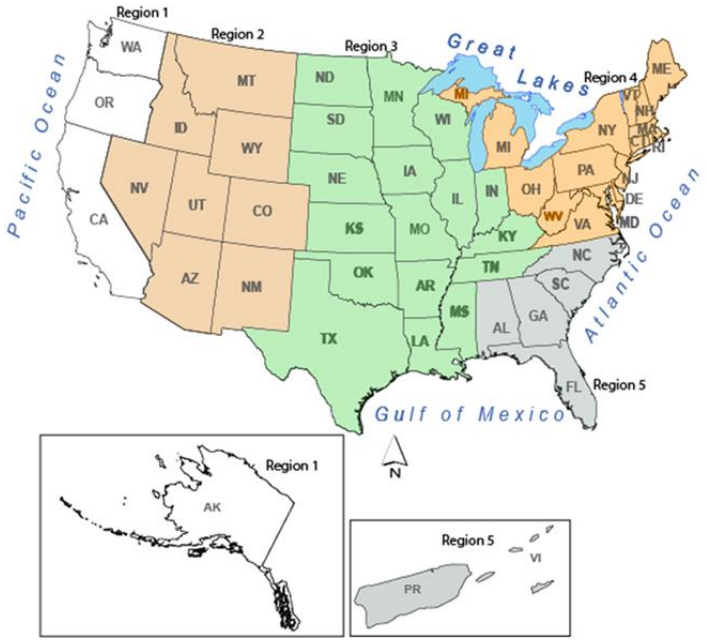
O:\Teams\NADP\NADP Lab\LAB Final Forms\QC acceptance limits

Appendix I2. HAL Control Limits

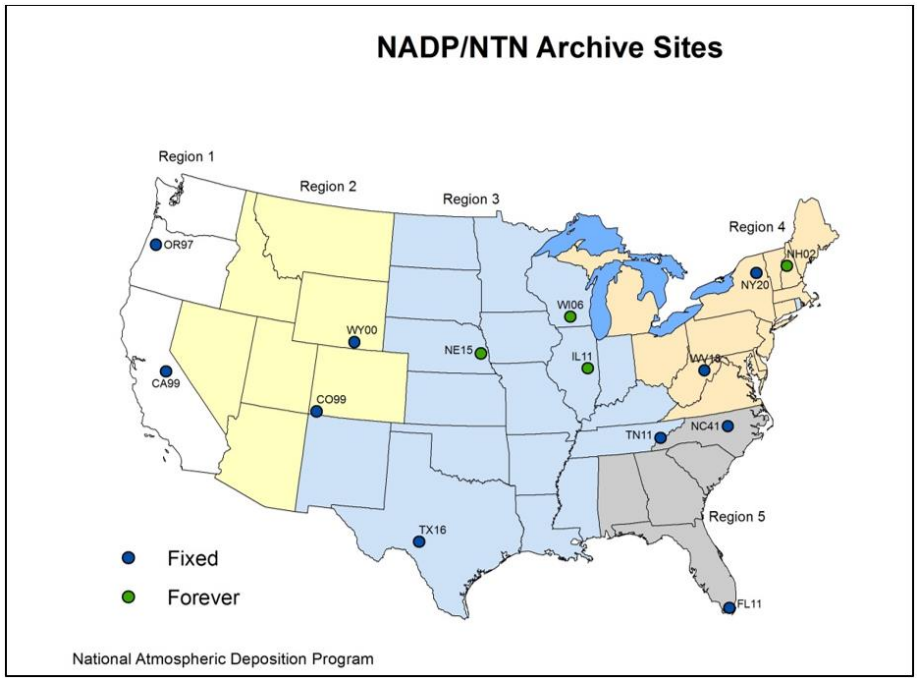
HAL Analytical QC		Rev 6/25/2020					
Total Hg Run ID	**LIMS ID**	**True Value (ng/L)**	**Criterion (% or ng/L)**	**Frequency of Testing**	**LIMS Criteria CL (1/3 criteria = WL)**		
Calibration blank (CB)	FCB19001	0.0	Mean < 0.5 ng/L	3 each analytical run	0.5/0.166		
Continuing Calibration Blank (CCB)	FCCB1901	0.0	<0.2 ng/L	After calibration; Every 10 samples	0.2/0.0667		
Ongoing Precison and Recovery (OPR5)	FOPR1901	5.0	80-120% (90-110% as calibration verification or recalibration	Prior to analyzing samples; Every 10 samples	1.0/0.333		
Digested Lab Reagent Blank (DLRB)	FRB19001	0.0	<0.2 ng/L	3 each analytical run	0.2/0.0667		
Digested Quality Control Standard (DQCS - 2nd	FQCS1901	8.0	80-120%	1 each analytical run	1.6/0.533		
Matrix Spike/Matrix Spike Duplicate MS/MSD	NA	NA	24% RPD	Every 10 samples	NA		
MS Recovery	NA	15.0	75-125%	Every 10 samples	NA		
Method Detection Limit (MDL) Standard	FMDL1905	0.5	80-120% (not batch QC parameter)	Weekly	0.1/0.033		
Methyl Hg Run ID	**LIMS ID**	**True Value (ng/L)**	**Criterion (% or ng/L)**	**Frequency of Testing**	**LIMS Criteria CL (1/3 criteria = WL)**		
Calibration blank (CB)		0.0	Mean < 0.05 ng/L	3 each analytical run	0.5/0.166		
Continuing Calibration Blank (CCB)		0.0	<0.1 ng/L	After calibration; Every 10 samples	0.2/0.0667		
Ongoing Precison and Recovery (OPR5)		0.3	65-135%	Prior to analyzing samples; Every 10 samples	1.0/0.333		
Distilled Lab Reagent Blank (DLRB)		0.0	<0.1 ng/L	3 each analytical run	0.2/0.0667		
Distilled Lab Fortified Blank (DLFB)		1.0	65-135%	1 each analytical run	1.6/0.533		
Matrix Spike/Matrix Spike Duplicate MS/MSD	NA	NA	35% RPD	Every 10 samples	NA		
MS Recovery	NA	0.5	65-135%	Every 10 samples	NA		
Distilled QC Standard (2nd source)/MDL Standard		0.5	65-135% (not batch QC parameter)	1 each analytical run	0.1/0.033		
HAL Supply QC					**HAL Calibration QC**		
Run ID	**LIMS ID**	**True Value (ng/L)**	**Criterion (% or ng/L)**	**Frequency of Testing**	**Calibration QC**	**Criteria**	**Units**
Sample Train Blank	2000XXXX	0.0	<0.8 ng/L (<0.08 ng per train)	1/week in bag for ≥2 days - 100 mL MQ	**Calibration Coefficient RSD**	≤15	%
Acid Bath Blank	2000XXXX	0.0	<50 ng/L	1/Acid Bath/week	**Calibrator Recovery**	85-115 (THg) 65-135 (MHg)	%
250 mL, 1 Land 2L PTGE Bottle Blank	2000XXXX	0.0	Mean bottle batch < 0.2 ng/L (NO bottle > 0.667 ng/L)	10/new lot (unless <100 then 5)	**Mean Cal Blank/System Blank**	<0.5	ng/L
Acid Preservative Blank	2000XXXX	0.0	<0.4 ng/L (15 mL sample)	1/Batch Acid Preserv prior to use	**Std. Dev. Calibration Blank**	<0.1	
THg Type 1 Water Blank	2000XXXX	0.0	<0.2 ng/L	1/purifier/week	**OPR** (as calibration verification)	4.5 to 5.5	ng/L

Appendix J. Archive Maps and Information

Appendix J1.NADP Archive Regions



Appendix J2.NADP "Forever" (all samples) and "Fixed" (monthly sample) Archive Sites



Appendix J3.NADP "Fixed" (Monthly Sample) Archive Sites

SITEID	Freq	Region	Start	AMoN	MDN	Operating Agency	Funding Agency	EEMS	Classification
CA99	10	1	12/8/1981			NPS	NPS	Yes	Isolated
OR97	4	1	4/26/1983			EPA	EPA	Yes	Suburban
CO99	4	2	4/28/1981		X	NPS	USGS	Yes	Isolated
WY00	8	2	4/22/1986			USFS	USFS	Yes	Isolated
TN11	12	3	8/12/1980		x	NPS	NPS	Ok*	Rural
TX16	10	3	6/26/1984			SAES-TX	USGS	Yes	Isolated
NY20	10	4	10/31/1978	x	x	SUNY-ESF	NYSERDA	Yes	Isolated
WV18	11	4	7/5/1978	x		USFS	USFS	Yes	Isolated
FL11	8	5	6/17/1980		x	NPS	NPS	Yes	Isolated
NC41	15	5	10/3/1978			NCS	NCS	Yes	Urban

Freq = number of archive samples currently in the long term archive from 1999-2012

AMoN/MDN = co-located sites with NTN

EEMS = Meets siting criteria and is well operated and maintained per EEMS site audits

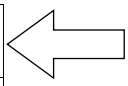
* Trees in violation on previous audit on date 11/3/15, but 2 trees in direct violation have been removed

Appendix J4.NADP Retention Schedule

Paperwork Retention Policy:

Keep current year and 1st year on site; 2nd through 6th years can be stored off site; at end of current year, dispose of 6th year.

CURRENT YEAR	1st YEAR ON SITE	2nd YEAR OFF SITE	3rd YEAR OFF SITE	4th YEAR OFF SITE	5th YEAR OFF SITE	6th YEAR OFF SITE
2019	2018	2017	2016	2015	2014	2013
2020	2019	2018	2017	2016	2015	2014
2021	2020	2019	2018	2017	2016	2015
2022	2021	2020	2019	2018	2017	2016
2023	2022	2021	2020	2019	2018	2017
2024	2023	2022	2021	2020	2019	2018



Dispose of 6th Year at end of Current Year

Sample Retention Policy:

- **NTN –** dispose 6th year at end of current year.
- **AIRMoN and AMoN -** dispose 2nd year at end of the current year.
- **Fixed/Forever NTN sites –** keep forever, may be stored off site.

Appendix J5.NADP Past Archive Policies

Past Sample Archive Strategy (Prior to 2019)

NTN Past Archive

Scope/Scale:

A running 5-year archive, going on 6 years, of all sites and sampling dates, was maintained. In addition, an archive of all samples from three sites (NH02, NE15, and IL11) extending back to initiation of sampling was maintained. Illinois State Water Survey (ISWS) also randomly archived 1 in 100 samples (not site specific) indefinitely (average of 2 per week – 100 samples per year).

Sample Description:

Whenever adequate volume (~ 120 mL) was available, up to 50 mL of precipitation was filtered upon sample receipt into 60 mL square polyethylene bottles for archival purposes.

Storage Condition:

The NTN archive had been kept refrigerated (4°C) except that the 1 in 100 and 3 long term sites (NH02, NE15, IL11) had been frozen.

AMoN Past Archive

Scope/Scale:

A running archive of all sites since beginning of AMoN.

Sample Description:

Remaining extract volume (approximately 5 mL) from the sorption cartridges in the original extraction tubes.

Storage Condition:

The AMoN archive has been frozen.

MDN Past Archive

MDN samples have not been archived.

Appendix J6.NADP Archive Preservation Study

It is believed that the former CAL at ISWS froze only the 3 long term sites, the 1 in 100 samples, and AMoN samples. It is not clear if they froze those samples as soon as processed or if they were frozen at the end of the year in which they were received. Although the CAL does not anticipate any detrimental effects to sample integrity from freezing all samples as soon as possible, due diligence will be taken to experimentally validate this. In addition, this study will determine if the sample integrity is maintained for 1-5 years of storage. To do this, CAL set up a 5- year study with identical samples that are both frozen and refrigerated and tested annually to identify any changes in the analytes from either preservation method. All NTN analytes will be quantified in this study. The details of this study is outlined in Appendix J.

In April 2019, 112 NTN samples with sufficient volume were saved in the cooler at 4°C for approximately 2 weeks prior to filtration. Therefore, the “original” NTN sample result may be slightly different than the Archive Time=0 samples. Each filter used in preparation of the study samples was pre-rinsed with sample. To avoid confusion, all the refrigerated samples were prepared first and then one day later all the frozen samples were filtered. The frozen and refrigerated samples have a different ID number to prevent mix-up during analysis in future years.

A single filter was used to prepare all the refrigerated or frozen aliquots of a single sample unless it became too loaded, and then a new pre-rinsed (with sample) filter was used. Filter apparatus were very thoroughly cleaned with Type I water between each NTN sample set and the filter was replaced. For each NTN sample 6 bottles (60 mL square) were prepared for refrigeration and 5 bottles for freezing following normal protocols. They were all filled to approximately the shoulder leaving room for expansion during freezing.

One bottle from each sample was placed in the following trays:

Archive Study 4/2019 Analytical Samples Refrigerated (for Time 0 measurement)

Archive Study 4/2020 Frozen; Archive Study 4/2020 Refrigerated

Archive Study 4/2021 Frozen; Archive Study 4/2021 Refrigerated

Archive Study 4/2022 Frozen; Archive Study 4/2022 Refrigerated

Archive Study 4/2023 Frozen; Archive Study 4/2023 Refrigerated

Archive Study 4/2024 Frozen; Archive Study 4/2024 Refrigerated

In April of 2019, preparation of all of the samples was completed, and all analytical measurements on the filtered refrigerated samples were made to establish the "time 0" initial concentrations. For each subsequent year's samples during the 2nd or 3rd week of April, the two trays for that year will be brought to the analytical lab cooler. This will include the refrigerated and frozen samples for each of the 112 NTN samples. As soon as the frozen samples are thawed all 224 samples will be analyzed for all NTN parameters. These samples are logged into a special LIMS project "Five Year Archive Preservation Study" so that all 5 years of data can be uploaded and stored under two 1900XXXX numbers for each sample (one for frozen and one for refrigerated) which are linked to the TUXXXXSW (NTN) number for the sample and the preservation type. All the refrigerated bottles also have a round brown sticker on the label to further differentiate them from frozen samples. After 5 years of this process, the CAL will have a full time series of data for 112 paired frozen and refrigerated samples from time 0 to 5 years later. The results will be evaluated to identify how the analytes change over time for both preservation techniques. Annual assessments of trends will be prepared and presented to QAAG/NOS.

Appendix K. Acronyms

Appendix K1. NADP CAL/HAL QAP Acronyms

QAP Acronym	Definition	QAP Acronym	Definition
AG	Agriculture Drive (lab)	LIMS	laboratory information management system
AIRMoN	Atmospheric Integrated Research monitoring Network	MDL	Method detection limit
AMoN	Ammonia monitoring network	MDN	Mercury Deposition Network
ASTM	American Society for Testing and Materials	MDS	Material distribution service
CAL	Central Analytical Lab (NADP)	mg	Milligram
CFR	Code of Federal regulations	mL	Milliliter
cm	Centimeter	MQ	Milli Q - (Type I water)
COA	Certificate of analysis	MS	Matrix spike
COC	Chain of custody	MSD	Matrix spike duplicate
CVAFS	Cold Vapor Atomic Fluorescence Spectroscopy	NADP	National Atmospheric Deposition Program
D	Dry	NELAP	National Environmental Laboratory Accreditation Program
DMAG	Data management advisory group (NADP)	ng	Nanogram
DOC	Demonstration of capability	NIST	National Institute of Standards and Technology
DQO	Data quality objective	NTN	National Trends Network
ECCC	Environment and Climate Change Canada	OIS	Office of Information systems
EFGS	Eurofins Frontier Global Sciences	OM	Occurrence management
EHD	Environmental Health Division	PETG	Polyethylene terephthalate copolyester glycol
ELN	Electronic laboratory notebook	PI	Primary Investigator
EPA	Environmental Protection Agency (U.S)	PO	Program Office
FB	Calibration blank (CAL) (F for LIMS function)	PO	Program Office (NADP)
FCB	Initial Calibration blank (MDN) (F for LIMS function)	PT	Proficiency test
FCCB	Continuing calibration blank (MDN) (F for LIMS function)	QA	Quality Assurance
FCRM	Certified reference material (F for LIMS function)	QAAG	Quality Assurance Advisory Group (NADP)
FIA	Flow injection analysis	QAC	Quality Assurance Committee (WSLH)
FL	Low level calibration verification standard (CAL) (F for LIMS function)	QAP	Quality Assurance plan
FLP	Low level calibration verification for high curve on ICP (CAL) (F for LIMS function)	QC	Quality control
FLRB	Lab reagent blank (MDN) (F for LIMS function)	QR	Quality rating
FLRB	laboratory regent blank (MDN) (F for LIMS function)	RDA	Records disposition authority
FM	Mid level calibration verification standard (CAL) (F for LIMS function)	RO	Reverse Osmosis (Type II water)
FMDL	MDL level QC sample	SOP	Standard Operating procedure
FOPR	Ongoing Precision and Recovery (MDN) (F for LIMS function)	T	Trace
FQCS	Quality control standard (F for LIMS function)	TOC	Table of Contents
FR50	Faux rain at ~ 50% of historical NTN analytes	USGS	United States Geological Survey
GRS	General Records retention schedule	UW	University of Wisconsin (Madison)
HAL	Mercury (Hg) Analytical Lab (NADP)	VPN	Virtual private network
HIPAA	Health insurance portability and accountability act	W	Wet (NTN)
HM	Henry Mall (lab)	WD	Wet dilute (diluted at receipt)
HR	Human resources	WDHS	Wisconsin Department of Health Services
IC	Ion chromatography	WDNR	Wisconsin Department of Natural Resources
ICP	Inductively coupled plasma	WI	Wet Incomplete (no pH/cond - NTN)
ISWS	Illinois State water survey	WMO	World meteorological organization
L	Liter	WSLH	Wisconsin State Laboratory of Hygiene
LDR	Linear dynamic range		