Laboratory Quality Assurance Plan
National Atmospheric Deposition Program

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National Atmospheric Deposition Program

The approved version of this document is located in OnBase – SOP Approved. Please confirm this copy is the latest version.

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 consistent with the 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 data, and oversee research activities related to atmospheric wet and dry deposition chemistry.

There are multiple monitoring networks within the NADP each with unique monitoring infrastructure, sample collection protocols and data quality objectives. However, as components of the 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 the NADP, oversees activities of all the networks and works closely with the network laboratories to publish the environmental monitoring data. The analytical labs aim to fulfill the mission of the NADP as described in its 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 NADP WSLH Management Team, the Program Office and the Quality Assurance Advisory Group (QAAG).

1.2 Historical NADP Analytical Lab 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 receive 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 Analytical Lab (NAL) 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 were: National Trends Network (NTN), Ammonia Monitoring Network (AMoN), Atmospheric Integrated Research Monitoring Network (AIRMoN) and the Mercury Deposition Network (MDN). The initiative was called Mercury Litterfall Monitoring Initiative (renamed Mercury Litterfall Network or MLN), which became an official network in 2021. These networks and the support laboratories have always been required to follow strict quality assurance (QA) and quality control (QC) procedures. See Table 1 for a Network Summary. The NAL has provided 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 central analytical laboratory (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. AMoN became an official network in 2010. WSLH began support and analysis for those three networks on June 1, 2018. AMoN and NTN are ongoing networks, while AIRMoN ended operations in September of 2019.

The WSLH also took responsibility for the mercury analytical lab on June 1, 2019 from Eurofins Frontier Global Sciences (EFGS) located in Bothell, WA. The NAL is responsible for site supply services, sample processing, analysis, and data validation for the Mercury Deposition Network (MDN). The EFGS lab ran a pilot study year in 1995, and then began analyzing NADP MDN samples from 1996 through May 31, 2019 as an official network.

A USGS pilot study of litterfall Hg dry deposition at MDN sites during 2007–2009 indicated that litterfall Hg monitoring could be accomplished at MDN sites and would yield meaningful

information about Hg dry deposition in predominately deciduous forests. The results of this 3-year pilot project were published in 2012 (Risch et al., 2012, Env. Pollut. 161: 284-290). The Hg laboratory at the USGS, Middleton, WI performed the analyses and served as a partner in this effort. Litterfall collection continued as a transition network during 2012-2014 at 27 sites, and a second publication (Risch et al., 2017, Env. Pollut. 228: 8-18) summarized results and examined temporal trends during 2007-2014.

In 2017, a motion was introduced in the NADP Executive Committee to make the Hg litterfall a permanent network. This motion passed unanimously but was later put on hold through intervention by the Prairie Research Institute based on concerns that the timing was not right. A later vote approved continuation as a transition network with plans to seek permanent network status in the future. In 2018, Doug Burns (USGS, Troy, NY) assumed management of the Hg litterfall transition network and operated it through 2019 with analyses continuing at the USGS Middleton, WI lab. In 2019, the Hg analysis laboratory shifted from the USGS to the NADP mercury laboratory at the WSLH in Madison, WI. For the 2020 litterfall season, NADP assumed full responsibility for operation and management of the network. At the spring 2021 NADP meeting, a motion was introduced and passed for the Hg Litterfall Network to become a permanent NADP network.

Ongoing emphasis on mercury in global, national, and regional contexts necessitates that the NADP prepare to provide more information on atmospheric Hg deposition. A current example is implementation of the global Minamata Convention on Mercury. Additionally, the NADP established a new science committee in 2019, called Mercury in the Environment and Links to Deposition (MELD). Mercury litterfall deposition is of great interest to MELD, because of relevance to forested ecosystems.

Historically, the analytical laboratories were differentiated as the central analytical laboratory (CAL) and the mercury analytical laboratory (HAL). The CAL encompassed the NTN, AMoN, and AIRMoN. The HAL encompassed the MDN and MLN. Since the CAL and HAL are within WSLH, they are now considered to be one lab and references to the CAL and HAL will be discontinued (at least in documents) and will be delineated by network instead. The labs are all in Madison, WI, under the same leadership and using many overarching QA goals/tools. This provides many efficiencies and enables better consistency among networks. A motion was passed at the Spring 2023 meeting to rename the two laboratories in combination as the NADP analytical laboratory (NAL).

In January 2024, a provisional sub-network of NTN was established to focus on the analysis of per- and polyfluoroalkyl substances (PFAS) in precipitation. The production and widespread global use of PFAS chemicals over the past 60 years has resulted in contamination of soil, surface and ground waters, the atmosphere and biota. A growing body of evidence documents that PFAS chemicals are potentially harmful to human health at environmentally realistic exposure levels. Studies over the past decade, including efforts at the NADP/WSLH, have shown

that atmospheric transport is a major environmental dissemination pathway for PFAS and that deposition via precipitation can represent a major source of PFAS to many terrestrial and aquatic environments. The establishment of the provisional sub-network reflected the maturation of protocols developed by WSLH/NADP staff for PFAS measurement in precipitation after 4 years of field and laboratory method testing in a pilot program supported in large part by US EPA. In spring 2026, the NADP will officially recognize the PFAS program as a formal sub-network (PFN) of NADP-NTN.

Table 1. NADP Network Summary

Network	Number of Sites (2026)	Sampling Frequency	Matrix	Analytes	Preservation
NTN	238	Weekly	Precipitation	pH, Conductivity, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, NO_3^{-}, SO_4^{2-}, NH_4^{+}, PO_4^{3-}	Refrigerate after Receipt and Filtration
AMoN	101	Biweekly	Air	NH_4^{+} (calculated NH_3)	Freeze after Receipt
AIRMoN	0	Event Based	Precipitation	pH, Cond, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, NO_3^{-}, SO_4^{2-}, NH_4^{+}, PO_4^{3-}	Shipped Iced, Refrigerate after Receipt
MDN	89	Weekly	Precipitation	Total Hg, Methyl Hg	1% HCl at Collection
MLN (Litterfall)	25	4 Weeks/retrieval in Leaf Season = 1-5 Retrievals per Season	Litterfall	Total Hg, Methyl Hg	Freeze after Receipt, Room Temp after Dried
PFN	15 (+ 4 pending)	Weekly	Precipitation	39 compounds; refer to EHD NADP PRC 16001 based upon EPA 533	Refrigerated upon receipt, frozen after filtering

1.3 Program Objectives

The primary program objectives of the NADP lab 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, litterfall and atmospheric passive samples, (c) data review/verification (d) data reporting to the PO, (e) maintaining 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 NAL. 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 referenced within this QAP. The supporting documents are not open access, however the Lab 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 I** for a table of acronyms.

1.4 Quality System Objectives

The Lab's quality system ensures data are of sufficient quality to reliably estimate spatial variation and temporal trends in atmospheric wet-deposition and ambient concentrations, 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 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 tracked in this table within the WSLH file system: O:\Teams\NADP\NADP Lab\Major Changes. Major changes are also covered in annual QA reports.

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 and ethics 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 NAL operates 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. The current organization charts are included in **Appendix A**. There are approximately 110 staff currently in the EHD of which approximately (depending on staffing levels/vacancies) 14 are associated with the NADP Lab. The EHD has a robust overarching QA program with which this QAP complies. There is also a Labwide Quality Assurance Committee (QAC) that functions to provide QA support for the entire WSLH. The NADP Program QA Supervisor attends EHD QA meetings. Additionally, 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), Office of Human Resources, and Office of the Director (administrative). WSLH support staff offices (e.g., Human Resources) work together with on-campus UW-Madison affiliates to assist in the hiring of staff, approval of contracts, purchases and/or to 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 laboratory 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. In general, most analytical operations take place at AG, while all the field related operations, shipping, receiving and supply cleaning are performed at HM. The main exception to this workflow is that of the PFAS Research Laboratory (PRL), where all operations take place at HM. The Program Office (PO) is also located at HM.

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 ***Labwide GENOP 1004 and 1101***.

2.6 NADP Lab Management

The NADP Lab is led by a team of managers and supervisors who report to the Environmental Health Division Director, Steve Strebel, who in-turn reports to the WSLH Director Dr. Rudolph Johnson. The Systems QA Manager, Dr. Martin Shafer; NADP Coordinator, Dr. Sarah Benish; NTN/AMoN Supervisor, Katie Blaydes; MDN/MLN/PFN Supervisor, Christa Dahman; Sample and Data Processing Supervisor, Zac Najacht; and Program QA Supervisor, Nichole Miller; all work together to manage the day-to-day laboratory operations. The Systems QA Manager and the Program QA Supervisor work independently of the day-to-day operational management of the lab. Dr. Benish is the NADP PI and Dr. Shafer is the NADP Co-PI. 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 the NADP are met. Monthly meetings are held involving all management from the Lab and the PO. Multiple managers and supervisors also are members of the NADP QAAG and/or Data Management Advisory Group (DMAG). Refer to **Appendix A** for the Laboratory Organizational charts.

2.6.1 Lab Supervisors

The lab supervisors oversee the analytical staff of their respective groups. The lab supervisors handle troubleshooting of instruments, ensure 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 supervisors' responsibility for the inductively coupled plasma optical emission spectroscopy (ICP-OES), flow injection analysis (FIA), ion chromatography (IC), cold vapor atomic fluorescence spectroscopy (CVAFS), Direct Mercury Analyzer (DMA), and tandem mass-spectrometer (LC-MS/MS) analysts. The lab supervisors review and/or create analytical lab documents, SOPs, and reports. The supervisors assist with a management review for EHD as well as network QA reports annually. The supervisors are also responsible for reviewing the monthly budget statements to ensure the lab meets overall program budget. They also are expected to present updates at NADP conferences and bring initiatives or concerns to QAAG or NOS.

2.6.2 Sample and Data Processing Supervisor

The sample and data processing supervisor provides oversight of the shipping and receiving staff. This supervisor 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 and review, analytical data review and validation, reporting to sites and publishing data to the PO are also overseen by the data processing supervisor.

2.6.3 Program QA Supervisor

The QA Supervisor is responsible for implementing and maintaining quality assurance procedures throughout the NADP laboratory and field operations. The QA supervisor works with

the other managers and supervisors to verify that QA procedures are followed by all staff. The QA supervisor is responsible for monitoring analytical and supply QC data for trends, management of documents, serving as the NADP QAAG Co-chair, conducting 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 supervisor is also engaged in WSLH division-wide and labwide initiatives and duties as a member of the EHD QA Team and the WSLH QAC. 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 lab, oversight of field/PO 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 and supervisors 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 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. Lab management should be informed by the lab staff of any staff needs or concerns in a timely manner.

2.7 Overall Responsibilities

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
- PT Program Participation
- 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
- MLN 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

- 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. 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, refer to the WSLH Knowledge Base in Team Dynamixhttp://slhicmsprod/. Specific position descriptions for all personnel are located in the main WSLH OHR 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 OHR has a checklist for new employees (http://slhicmsprod/administrative-services/human-resources/) which includes lab-wide training requirements. The NADP also has a new employee training checklist 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 or supervisor guides the new employees through the checklists. Employees are also required to review safety checklists with a safety officer or manager/supervisor 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 are required to review the plans for both locations.

2.9.2 Data Integrity Procedures

The integrity of NADP data is of utmost importance. To ensure this, all employees must sign off on and follow the "Data Integrity, Ethics, Data Documentation Procedure" for the WSLH, Environmental Health Division (***EHD Division-Wide GENOP 029*** located in OnBase). 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. Trainees review the applicable SOPs as well as the instrument manual(s). They observe an experienced analyst in preparation of samples and operation of the instrument. They then work under the direct

supervision of the experienced analyst until familiar with the analytical procedures and successfully complete 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" (IDOC) after adequate training on the analytical method and document the results on the DOC Certification Statement. This is required for new employees or for employees who have not completed an ongoing DOC for a particular method in more than 13 months. The IDOC includes: independently setting up the instrument, including preparation of standards and reagents, 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 four replicates of a spike solution that they prepared. When initial DOC criteria have been satisfied and the experienced analyst, QA supervisor and Lab supervisor are confident that the employee is thoroughly familiar with the test, that employee is allowed to work independently on that platform with only routine supervision. In addition to the analytical DOCs (for LC-MS/MS, CVAFS, DMA, 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. All Lab DOC procedures are described in greater detail on the applicable forms at: O:\Teams\NADP\NADP Lab\LAB Final Forms\DOCs. Initial DOCs for MDN and MLN are detailed in the method SOPs.

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 replicates of a spike solution prepared by the analyst. 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

2.9.6 SOP Updates

Analysts are responsible for notifying the QA supervisor of needed updates to SOPs and must assist with the revision process. OnBase is the system for tracking SOP modifications. OnBase tracks who is doing the editing or leaving a note as long as the SOP is saved. If a change is needed, staff members should log into OnBase and then make a "review note" (looks like a post-it note) on the SOP listing what needs to be fixed, or just start the edits by moving the SOP from "draft parking" to "edit" queue. When a new version of a SOP is finalized, the version tracking table in the SOP documents all the major changes, and all analysts must document their review of the new or updated method on their annual SOP

review sheet. OnBase automatically changes the version number and records who performed the editing and approving.

2.9.7 Annual Document Review

At a minimum, all NADP employees must review and document in the Annual Review Canvas course all of the following NADP, WSLH EHD, or WSLH Lab-wide documents:

- HIPAA Refresher
- Safety Checklist
- Chemical Hygiene Plan
- Data Integrity, Ethics, and Data Documentation Procedure
- Emergency Response Plan
- Nonconforming Event Management Policy and Procedure
- Accident Reporting
- NADP Lab QAP
- NADP NTN, PFN, AMoN, MDN, and MLN Analytical SOPs (as applicable to their position)

2.9.8 NTN and AMoN Annual Rotation

If possible, the NTN and AMoN analysts will rotate analytical platforms annually at the supervisor'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 have elapsed since proficiency was demonstrated, an initial DOC (rather than an ongoing DOC) must be completed for that method. AMoN preparation DOC for the current analyst is demonstrated by the routine batch QC that is required by the method. For other preparation staff, if more than a year has passed since they prepared AMoN samplers, a new IDOC will be necessary before samplers they prepare are sent out in the field. In the PFAS Research Lab, several chemists are cross-trained on the core instrumentation (LC-MS/MS and autoextractors) to ensure uninterrupted coverage and resilience.

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 supervisor or QA supervisor (as applicable). The QA supervisor will ensure that the DOC documentation is complete and meets the criteria. The lab supervisor will be responsible for general training records. Most training documentation will be filed in the

personnel training files maintained by each supervisor. DOC documentation is maintained by the QA supervisor. Since August 2020, there has been a requirement that all new employees also are required to watch the QA & You brown bag video and submit an attestation statement to Human Resources. Also, new training required for use of OnBase to access SOPs is available in Canvas. There is also a required training, video and training form, to have user access to the Nonconforming Event Management (NCEM) software, MediaLab.

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. There is also the opportunity to attend training or utilize resources through the UW, 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 WSLH 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 Chemical Hygiene Plan

The WSLH has a detailed “Chemical Hygiene Plan and General Laboratory Safety Plan” for each facility (***LABWIDE SAFETY 102 – Ag Drive*** and ***LABWIDE SAFETY 202 - HM***), which contain comprehensive information on general lab safety procedures and operations, including chemical storage, waste disposal, safety showers, fume hoods, controlling exposure, employee safety training, housekeeping, emergency procedures, and more. It also contains important safety-related information including policies on eye protection, fire extinguisher training, footwear in lab areas, glove use, and protective clothing. Included in the SOP are links to UW-Madison employee health and safety information. To ensure the safety and well-being of all WSLH personnel, new employees must become familiar with safety precautions before working in the laboratory, and all employees must review the Chemical Hygiene Plan annually.

3.2 Emergency Response Plan

Employees are responsible for reviewing the Emergency Response Plan (***LABWIDE SAFETY 101 – Ag Drive*** and/or ***LABWIDE SAFETY 201 – HM***) on an annual basis depending on which

building location applies to them. This SOP details the procedures for foreseeable emergencies, identification of event specific gathering points, procedures for mobility- impared personnel, procedures for information dissemination to all personnel, and guidelines for floor captians.

3.3 Safety Checklist

A key tool in safety training is the WSLH Employee Safety Checklist (***LABWIDE SAFETY 300***) 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.

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 using Acumatica 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 through Acumatica, 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 supervisors will assist in this endeavor by purchasing supplies and monitoring those that need to pass QC checks prior to use. Managers and supervisors will track budgets to ensure that purchases will meet the NADP budget expectations. Bottles, test tubes, filters, bucket lids, 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 the amount is >$25,000 or three quotes are required if the amount is between $5,000 and $25,000. The lab supervisors or director facilitate capital equipment requests. All capital equipment requests must be approved by NADP Managers/Supervisors, 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) maintains a number of quality objectives to insure the integrity, security and reliability of our systems. OIS Document located at: \\SLHFILE\GRP\OIS\OIS Administration\Compliance\Z_Other\OIS Quality Assurance.docx

The Quality Objectives include:

- A state-of-the-art data center with exceptional security, redundant connectivity and a climate controlled environment that meets the following certifications:
    - Type 2 SSAE 18 (SOC 1)
    - SOC 2 Type 2 (Security and Availability Trust Principles)
    - HIPAA
    - PCI DSS
    - ISO 27001
    - U.S. EU Privacy Shield

- Whenever possible, independent test systems are created alongside production to allow a safe environment for training as well as a place where changes can be tested prior to being put into production.
- The use of ITILv4 (Information Technology Infrastructure Library) and risk management frameworks to provide continual process improvement and apply best practices such as Change Management.
- Utilizing a risk-based approach to backup and recovery planning, taking advantage of multiple recovery options when it makes sense to do so (e.g. point-in-time recovery for databases; shadow copies at set intervals during the day) to improve backup and disaster recovery efforts. Backups to tape media utilize a grandfather-father-son rotation scheme and are kept for a corresponding timeframe of weeks, months, or years. These tapes are stored in "media proof safes" that are UL-125 rated (will not exceed 125 degrees Fahrenheit).
- Multiple, redundant network paths for our servers and workstations employing a secure IPSEC tunnel over a fiber-optic ring owned by the "Metropolitan Unified Fiber Network (MUFN) Consortium" <https://mufn.org/> (of which we are a voting member) back to the UW-Madison campus and protected behind firewalls. The UW-Madison is our Internet service provider. Secured VPN service with Remote Desktop Connections (RDC) is used for remote access to enterprise resources.
- Policies, standards, and procedures governing user account creation, system access, personal information protection, and the appropriate use of information systems and resources including the use of HIPAA's "minimum necessary standard" whereby users are only granted the minimum access necessary to do their jobs.
- Inventory and asset management including anti-malware/antivirus, vulnerability scans, and routine patching for operating system and 3rd party patches (e.g. all servers are patched within 30 days of critical/security operating system patch releases).
- When computers, drives, and media are no longer useful or usable they are sanitized and/or disposed of in a manner consistent with UW-Madison HIPAA policy.
- *(See the "WSLH IT Security Plan" for details and additional items.)*

Special protections for our Instrument Workstations:

- Instrument workstations typically cannot run the latest operating system patches for fear of breaking the acquisition/analysis software. These are protected by 2 different, segregated VLAN's (virtual networks) with firewall rules:
    - **Instrument VLAN** - contains instrument workstations capable of running 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 our LIMS systems (e.g. Epic, WindoPath, ChemWare) to improve data integrity and increase laboratory productivity.
- 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 our servers to a shared drive location). OIS staff work with laboratory staff to ensure the correct data are being backed-up. The shared drive location is then backed-up to tape using our routine processes. It is the laboratory's responsibility to ensure any new data storage locations on the local machine are being backed up to our servers and to work with OIS to ensure ongoing backups work as expected.
- We also maintain "bare metal" backups of our instrument workstations using disk imaging software on an annual basis or whenever laboratory staff notify us of a change to the workstation. It is preferred to take a backup image prior to any vendor changes in case these changes need to be rolled-back. When the work is complete and verified, another backup image should be taken to allow future disaster recovery. It is the responsibility of laboratory staff to notify OIS in advance of these changes so the work can be scheduled. These backups are maintained to allow recovery of the PC configuration in case of a catastrophic loss of hardware at the PC level.
- All vendor technicians are required to have their removable media scanned before it can be inserted into the instrument PC to prevent the spread of viruses and malware.

5.2 NADP LIMS

The lab utilizes a custom-made LIMS system. The LIMS is made up of multiple components that are utilized by personnel depending on their roles. These are the systems:

- **Benchchem** – used to add QC samples, review QC results, print additional bottle labels, look up sample results for all networks, complete AMoN extractions and WI/WD preparation (balance interface), run queries and reports
- **Instrumental Chemistry** – used for upload of instrument results, has many functions that are the same as in Benchem
- **NADP Address Book** – used to record site information (status, address, contact, equipment type)
- **NADP Shipping –** used to ship supply boxes to network sites, track needed and filled supply requests, and print supply box labels
- **NADP Data Entry** – used to assign a unique ID to each sample for all networks and to enter data from the field form. Also used to track supply requests and shipments.
- **NADP Data Review** – used to review sample field/lab data and determine quality rating for each sample. Used to generate/send data reports to sites. MLN is using a spreadsheet report for now.

- **NADP Data Management** – Only used to send AMoN reports, but soon will be able to do through the Data Review program.

5.3 EHD LIMS

Samples for PFN are tracked through Clinisys Laboratory Solution (CLS), which is the LIMS used by most other departments in EHD. Any NADP LIMS identifiers that exist for samples and QC are connected to the PFN sample metadata within CLS LIMS. PFN sample PFAS data from CLS will be reported to NADP Data Management in an electronic format and combined with their associated NTN field data and made available on the NADP website. It is expected that all of NADP will transition to CLS in 2026-2027. See ***EHD DIVISION-WIDE QA PLAN 001***, Section 1.16 for more information about CLS.

6. Records

6.1 QA Document Maintenance

All documents related to laboratory processes are required to have appropriate document control (unique title, version number, effective date and page numbers at a minimum). This includes SOPs, forms, bench sheets, plans, and reports. Laboratory staff are required to read the Lab QAP and relevant SOPs annually and when there are major changes. The QAP and analytical SOPs will be thoroughly reviewed by a subject matter expert for updates and corrections annually. Non-analytical SOPs will be reviewed for corrections at least every 2 years. All SOPs are stored in OnBase document control software, where changes and approvals are tracked. Versions are numbered and dated; previous versions are automatically placed in the electronic archive for reference and can be compared to identify changes. The QAP and all SOPs will include a version table in which any substantial changes to the content will be detailed for each version for future reference. OnBase can generate a list on demand showing all NADP SOPs and their current status. An SOP list is also posted on the NADP website. A copy of any NADP SOPs can be obtained at any time upon request.

6.2 Standard Operating Procedures

SOPs are written and maintained for all NADP functions. These are stored in WSLH OnBase which can be accessed by all staff on the WSLH homepage.

In addition, there are SOPs that apply to operations covered by this QAP that are applied at three different levels within WSLH: Lab-wide, Division-wide and NADP Department-specific SOPs – all can be found in OnBase.

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 supervisor and tracked: O:\Teams\NADP\NADP Lab\QA\Lab Notebooks. The lab is 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 stored online: O:\Teams\NADP\NADP Lab\NADP ELN for stocks and prepared solutions. The notebook contains a unique solution ID, date prepared, date expires, use of solution, and analysts initials.

6.4 Instrument Records

The QA supervisor 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 B1** 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. The 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 supervisor 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. In addition, ***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 Lab relies 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 appropriate lab supervisor 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 recorded in the instrument

logbook and should be included in nonconforming events management records for repeated issues. 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, lid 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. The HM RO system is disinfected annually by NALCO. The systems and all applicable numbers are listed in the equipment log O:\Teams\NADP\NADP Lab\Equipment\NADP Equipment Log.

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 has 5 Type I water systems - located at HM 135, HM 303, HM 511 and two 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 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 (and is not really necessary for NADP analytes). 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. If the resistivity is below 18 MΩ-cm corrective action is taken and a manager or supervisor is notified. If the resistivity reading or analytical data (i.e. unresolved method blank issues) does not meet criteria an alternate Type I system that meets criteria is used until the issue is resolved. If a system appears to be faulty water blanks should be collected and tested for applicable analytes.

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. The certified thermometer information is recorded in the first row of the following spreadsheet O:\Teams\NADP\NADP Lab\QA\Thermometer Verification\NADP Thermometer Calibration Worksheet.xlsx. The certified thermometer is placed in the liquid

corresponding to the thermometer being tested, and allowed to stabilize. If the liquid container is sealed, the probe can be suspended between the shelf slats. The stabilization time may be increased by this method due to the blowing fans. The temperature reading from both thermometers is recorded in the spreadsheet. The difference between the two temperature readings is calculated. 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 replaced. 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. Samples should be relocated if the issue cannot be solved quickly. For more details on the verification process, see the associated SOP, ***EHD NADP LAB QA/QC 206***.

7.4 Analytical Balances

Analytical and top-loading balances are monitored for proper operation and accuracy by using 3 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 10 years. The NTN (WI/WD syringe filtration), AMoN (extraction) and MDN (login) balances are directly interfaced with the NADP 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 done by the gravimetric method. 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 supervisor maintains. For more details on the verification process, see the associated SOP, ***EHD NADP LAB QA/QC 204***.

7.6 Volumetric Flasks

All class A plastic volumetric flasks are verified at least once annually with two replicates of the expected volume. Testing is done gravimetrically where the analyst takes a tare weight of the flask, fills it with room temperature water up to the indicated line, and places it back on the scale to record the weight/volume. If there are issues with a flask, and retesting provides the same results, the flask will be removed from use for standards and reagents. Another flask will be purchased, if need be, and verified upon receipt. For more details on the verification process, see the associated SOP, ***EHD NADP LAB QA/QC 205***.

7.7 Traceability of Measurements

7.7.1 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 request an order via our supply tracking spreadsheet when those dates are approaching. The staff person checking in or preparing a chemical is responsible for labelling 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. ChemManager+ is also used for tracking inventory of stocks via a barcode system and all chemicals are logged into the system upon receipt.

7.7.2 NTN and AMoN 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. 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-22-S13 for the 13th stock logged in 2022.

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. 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-22-P35 for the 35th prepared chemical mix in 2022.

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 into the electronic COA file (O:\Teams\NADP\NADP Lab\Certificates of Analysis). If downloaded from the manufacturer, it can be saved directly to our files using the NADP code as the file name and adding the chemical name in if possible. For example, file name of "NADP22_S19_potassium chloride". A hard copy is also saved in a binder located in lab 119 at AG. 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.

7.7.3 MDN/MLN Standard and Reagent Tracking

The MDN lab 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 MDN lab 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, then 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.

7.7.4 PFN Standard and Reagent Tracking

PFN tracks reagent chemicals, stock solutions, and SDS using ChemManager+, which is a chemical inventory platform implemented by UW-Madison (https://chemmanager.wisc.edu/). Mixed intermediate, working standards, and mixed reagents are recorded in a spreadsheet stored in M:\EHD\PFAS Research Center\Standards Documentation\Standard Prep and Receipt Log.

7.7.5 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. For MDN analysis, these peer review sheets are stored in: M:\EHD\ESS(4900)\ESS Inorg(4910)\METALS\Clean Room\TEMPLATES\Mercury TemplatesData 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. For PFN analyses, a bench sheet template is provided within the analytical SOP (***EHD NADP PRC METHOD 16001***) and a peer review coversheet template is stored in M:\EHD\PFAS Research Center\Templates\Final.

8. Supply QC

Each network under the NADP 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 lab must be consistent across and within sites. The laboratories must provide clean and validated supplies for NTN, MDN, AMoN and MLN.

8.1 Supply Blanks

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

- Test tubes (for instrument autosamplers)
- NTN collection bucket lids
- NTN (1L) HDPE sampling bottles
- NTN 60 mL HDPE sample bottles
- NTN polyethersulfone filters and syringes
- NTN bucket and lid storage bags
- NTN sampling bags
- AMoN Radiello cartridges, Radiello cores and glass shipping jars
- MDN preservative HCl acid
- MDN PETG (or PET) 250 mL, 1L and 2L bottles
- MDN sample trains – funnels and thistle tubes
- PFN centrifuge tubes
- PFN autosampler vials
- PFN reagents
- PFN syringe filters
- PFN 250, 500, and 1000 mL HDPE bottles

8.2 New NTN, AMoN, MDN, MLN, and PFN Supply Assessment

New lab supplies that are not routinely pre-washed must meet "Lot QC" requirements per ***EHD NADP LAB QA/QC 200*** "NTN and MDN Supply QC". 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 ***EHD NADP LAB GENOP 405*** "MDN Supply Preparation".

8.2.1 NTN 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. New syringes and syringe filter lots are also tested before use following the SOP and Supply QC Log In and Frequency sheet. Disc and syringe filter blanks (on-going) are also performed regularly (per SOP).

8.2.2 NTN 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 QC samples are in the same tubes.

8.2.3 NTN/AMoN 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 C** 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 samples may be tested, or the entire lot may be rejected and returned to the manufacturer. If the second test fails, further testing can be tried but if an alternate cause is not found then the lot must be rejected. For batches of filtering or bag supplies greater than 1000, a minimum sample set of 20 QC checks are analyzed prior to use unless there are serious supply chain shortages to consider.

8.2.4 MDN New Bottle Testing

PETG (or PET) bottles are purchased in large lots and must be tested prior to being accepted for use within the MDN. Refer to ***EHD NADP QA/QC 200*** and Supply Lot Approval QC Frequency Table in **Appendix D** for specifics. 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 MDN 1% HCl Preservative acid

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

8.2.6 MLN New Supply QC

When a new supply of MLN netting is purchased, it is extracted to check for background mercury contamination before use. A mercury result from the netting extract of less than the LOQ is approved for 100 cm^2 of netting extracted in 100 mL of ultra-pure water. MLN bags have already been tested and determined clean. If bag supplier changes they will need to be tested for acceptability.

8.2.7 PFN New Supply QC

Trip blank, field blank, and field spike controls are collected by all PFN site operators twice per year. The liquid samples and the associated bags are assessed for PFAS recovery and background to ensure that target analytes are not lost to or contaminated by the bags that are used for routine NTN sample collection. See "PFAS-2214_Semi-annual_QC_Instructions" provided by the PO on the NADP website.

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 D** for details of all ongoing supply QC frequencies and criteria. Analysts are also asked to notify the QA supervisor 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. 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 ***EHD NADP LAB GENOP 405.***

8.4 AMoN Supply QC

Only Passive Diffusion Samplers (PDS) approved by the NADP are used for sampling (currently using ALPHA products, but Radiello® products historically). As outlined in **Appendix D**, "AMoN Supply QC", the filters, both acidified and unacidified, are tested as well as a fully prepared sampler and the water used for extraction. Also monitored is the background level of ammonia in the hoods in which the AMoN supplies and samples are processed. Refer to ***EHD NADP LAB GENOP 411 Preparation of Passive Ammonia Diffusive ALPHA Samplers*** and ***EHD NADP LAB METHOD 502 Determination of Ammonium by FIA*** for more details of AMoN supply preparation and analysis.

8.5 General 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 D** for example), to fill in the "Client" and "Description" fields. A barcode label sticker 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, AMoN, MLN, and PFN is contained in the applicable SOPs. For sample log-in specifics refer to ***EHD NADP LAB GENOP 100 - Sample Log In and Data Entry***. Samples are logged in by entering information from the field forms into the NADP 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. Where PFAS data is needed, excess unfiltered NTN sample is forwarded for PFN processing. MDN samples are collected directly into the acid-charged sample bottle, which after

receipt at HM is delivered to AG for digestion and analysis. AMoN samplers are shipped and received in anti-static bags inside of boxes from HM to AG. MLN samples are received in plastic bags and kept frozen either at HM or AG until processed. Samples with long hold times at that lab are not generally invalidated due to the fact that they are being stored in a controlled environment and likely have already undergone some processing. For example, NTN samples will be filtered; AMoN, PFN, and MLN samples are frozen; MDN samples are brominated. This differs from samples stored for an excessive amount of time in the field (see Table 2) which could be at variable temperatures and without any processing. In those cases, it is appropriate to invalidate the sample.

Table 2. Network Field and Lab Deployment and Hold Times as of 1/1/2022

Network	Preserv.	Prep	Field Deployment Time Flagged	Field Hold Time Flagged/Receipt	Lab Hold Time Flagged/Analysis
NTN	4-6°C (at lab)	Filtration	>8 days, 2 hours = QRC (invalid)	>16 days after off date = QRB >60 days after off date = QRC (invalid)	>30 days from receipt = QRB
PFN	-20°C or 4-6°C (at lab)	Filtration, Extraction	>8 days, 2 hours = QRC (invalid)	>16 days after off date = QRB	>90 days from collection (if frozen) = QRB
AMoN	Frozen (at lab)	Extraction	>15 days = QRB >30 days = QRC (invalid)	>60 days after off date = QRC (invalid)	>30 days from receipt = QRB
MDN	1% HCl (in field)	Oxidation /Distillation	>8 days, 2 hours = QRB >21 days = QRC (invalid)	>16 days after off date = QRB >60 days after off date = QRC (invalid)	>60 days from bromination = QRB

Note: QR stands for Quality Rating, and A, B, and C are the different levels of QR codes (A = no issues/valid, B = minor issues/valid, C = major issues/invalid).

9.2 Chain of Custody (COC)

Samples arrive at the lab 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 and MLN) 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 (if applicable, such as fixed or forever sites). AMoN sample bags (with anti-static bags 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 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 ***EHD NADP LAB GENOP 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). NTN aliquots for PFN are stored at -20°C in 250 mL HDPE. AMoN sample extracts are stored in conical tubes in the refrigerator overnight before analysis. After acceptable analysis AMoN samples are sent to HM to be stored frozen.

The acidified and brominated MDN samples are discarded after the sample data are published to the PO. For NTN the remainder of the analytical NTN sample is returned to HM for archiving. Certain NTN samples will also have a full extra 60 mL archive sample that is collected at the filtration step. See archive section for specifics. AMoN samples are kept frozen in the original extraction or analysis tubes. The remainder of the MLN composited sample is kept frozen at AG.

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. 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 as possible. 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. Samples are analyzed for pH and conductivity and then filtered within three business day of receipt (assuming receipt Monday – Friday) if possible.

9.4.1 NTN Sample Processing

All NTN samples over 4 mL are filtered prior to analysis (as of January 2020 WI/WD change). For the fixed and forever archive sites, 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 stored frozen. For all other NTN sites (unless part of a special study), a single 60 mL bottle is filtered, all analyses are completed, and then any remaining sample is logged into archive software and placed in the refrigerated archive. Samples will 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. A WI sample will be analyzed for all parameters (on diluted sample) except pH and conductivity. See Table 3 for more information. The dilution of WI and WD samples allows analysis by FIA, ICP and IC for all NTN analytes. See **Appendix E** 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). Long-term archive samples are frozen once the storage tray is full. Refer to Table 2 above for network

sample details and Table 3 for sample handling based on volume. Several of the field and lab hold times were updated beginning with January 2022 samples – the current requirements are provided in Table 2. Table 3 outlines how samples of differing volumes are handled.

Table 3. NTN Volume Assessment

NTN Sample Type	Abbreviation	Volume	Filtering	Dilution	Analysis
Dry	D	0 mL	No	No	None
Trace	T	≤ 4.00 mL	No	No	None
Wet Incomplete	WI	4.01-13.50 mL	Syringe	Yes to 15 mL	All except pH and conductivity
Wet Dilute	WD	13.51-27.50 mL	Syringe	Yes to 15 mL if less than 15 mL after pour off	All NTN analytes
Wet	W	≥ 27.51 mL	Large Disc	No	All NTN analytes

9.4.3 NTN Sample Collection Deployment Period

Bagged 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 > 8 days and 2 hours (194 hours) is coded as invalid (QR=C).

9.4.4 NTN Hold Time

All NTN sample analyses, except for pH and conductivity, are to be completed within 30 days of sample receipt at the lab. If lab analysis occurs over 30 days from receipt, then an "h" (for handling) notes code and QR = B will be applied in the lab data (on the web this will display as valid with an "h" notes code). The pH and conductivity analyses are to be completed within 3 business days of sample receipt if possible. 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. 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 ***EHD NADP LAB GENOP 412***. 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 F** for sample notes and QR code information. After an overnight extraction in high-purity water, samples are analyzed for ammonium by FIA (see ***EHD NADP LAB METHOD 502***).

9.5.2 AMoN Sampler Deployment/Storage

Prepared passive samplers (refer to ***EHD NADP LAB GENOP 411*** for AMoN sampler preparation) are

placed into anti-static bags 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 anti-static bags and Ziploc bags and sent back to the lab in the dedicated shipping box.

9.5.3 AMoN Sample Hold Time

AMoN sample extraction and ammonium analysis must be completed within 30 days of receipt at the lab otherwise result in an "h" notes code and quality rating QR=B for delayed sample processing. Refer to Table 3 above for network sample details.

9.5.4 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 over 15 days is still valid but is qualified for long sampling period ("e" flag, QR=B) and if deployed over 30 days will be deemed invalid (QR = C).

9.5.5 AMoN Travel Blanks and Duplicates

Each AMoN site will receive at least 3 travel blanks (TB) and 3 duplicate sets per calendar year. Sites desiring more frequent QC samples can contract with the lab for a different frequency. 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 bag. They store it for the deployment period and then return it with the deployed sampler(s). Duplicate samplers are two samplers designed to be deployed at the same time at the same site to measure precision.

9.5.6 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 3 years to ensure ammonia scrubbing capability. Ammonia levels are monitored by deploying AMoN passive samplers in the hoods for two-week periods. If hood blanks are trending high, then the hood filters may need replacing sooner. HEPA filters in the tube and jar drying hood are replaced every 5 years. The filter replacements are recorded here: O:\Teams\NADP\NADP Lab\Equipment\Ammonia Hood Filter Tracking.xlsx.

9.6 MDN and MLN Sample Receiving and Processing

MDN and MLN samples are tested for total mercury (THg) (and previously methyl mercury (MeHg)) analysis are received at HM, logged into LIMS, assessed for open bags, leaks (pH checks on water in the bag), and sample weights are obtained. Prior to May 2022, methyl mercury subsamples were taken from applicable MDN sites. Samples are sent via shuttle to AG for preparation and analysis. MDN samples are collected at each site on a weekly schedule. MLN samples are collected monthly over the Litterfall season which varies depending on location and types of trees.

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, the lab supervisor has checked for missing sample results, and the data is set to publish by the PO.

9.6.2 MDN Sample Preservation

Samples are collected in the field directly into acid (1% v/v HCl) pre-charged PETG (or PET) bottles

and thus mercury is stabilized immediately upon collection.

9.6.3 MDN Sample Volume Assessment

Sample volumes less than 1.7 mL (prior to 2026, 1.5 mL) of actual precipitation (plus ~20 mL of pre-charge thus 21.5 mL total or lower) are considered dry and are not analyzed for total mercury. Sample volumes greater than 1.7 mL are analyzed for total mercury. Prior to May 1, 2022 if the precipitation volume was greater than 25 mL a split for methyl mercury was taken if the site was a MeHg site. That practice was discontinued May 1, 2022 as directed by NADP Executive committee.

9.6.4 MDN Hold Time

MDN analyses are to be completed within 60 days of bromination in order to meet the EPA METHOD 1631E requirement that all samples are analyzed within 90 days of collection, which includes maximum deployment and holding time. 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 > 30 days is coded as valid with issues (QR=B), and with a deployment of over 60 days is invalidated. A sample received over 60 days after date off will be invalidated (QR=C).

9.6.6 MLN Sample Processing

MLN samples are sent to AG from HM after login or in batches. They are stored frozen when at HM or AG. At AG, they are oven dried and ground for analysis. The excess sample is saved until sample data packets are peer reviewed, uploaded to LIMS, the lab supervisor has checked for missing sample results, and the data is set to publish by the PO.

9.6.7 MLN Sample Preservation

Samples are collected in the field in netting within a bin and are transferred to clean plastic bags and sent to the lab. Field operators should return the samples to the lab within 2 months of collection. After drying, samples are stored at room temperature. All MLN samples are processed unless they arrive moldy.

9.6.8 MLN Hold Time

MLN analyses are to be completed within 6 months of drying. Refer to MLN SOPs for details.

9.7 PFN Sample Receiving and Processing

9.7.1 PFN Sample Receipt and Login

For samples requiring PFAS analyses, excess unfiltered NTN samples are returned to HM with a COC. The samples are placed in a refrigerator at 4°C and documentation is stored as described in 9.2. Staff from the PFAS lab collect the returned samples from the refrigerator weekly. Samples with a volume >50 mL are logged in according to ***EHD NADP PRC GENOP 001***. All samples are associated with the NADP LIMS identifiers (e.g., T2601546) and CLS identifiers (e.g., 833425011). Copies of the NTN FORF are labeled by PFAS staff with additional stickers and associated with the samples in CLS.

9.7.2 PFN Filtering

Samples are batched and individually vacuum filtered through quartz fiber filters within 14 days of log in. Filters are used just once. The filter funnel and vacuum flask are made of polypropylene and are

cleaned with ASTM Type I water and methanol in between each sample. The filtered sample is distributed into 250 mL HDPE bottles (up to 2 bottles per sample) and stored frozen at -20°C until extraction.

9.7.3 PFN Extraction

Batches of 6 samples, 1 method blank, and 1 laboratory control are spiked with isotopically labeled surrogates and processed through solid phase extraction. This extraction purifies and concentrates the analytes and produces a 1 mL methanol-based sample extract. These extracts are stored at -20°C until analysis.

9.7.4 PFN Hold Times

All field hold times and criteria that apply to NTN samples are observed by PFN. Contamination noted for NTN will be noted for PFN, but will not automatically invalidate PFAS results. All other field notes and quality ratings are consistent between the two networks. The analytical hold time is ≤90 days from collection when samples are frozen. Hold time exceedance will be flagged but will not automatically invalidate the results.

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 when possible and caution is taken when aliquoting samples.

10.2 Instrument Calibration

Each NTN and AMoN 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. Due to the fact that 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. The 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 to verify acceptance. The NTN and AMoN 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. For mercury, 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 NTN and AMoN Initial QC Standards

Initial QC standards are analyzed at the beginning of each analytical run. See **Appendix G** for the table outlining most of the QC standards and control limits (NTN standard FCRM is not listed on those tables as the expected values constantly change). LIMS IDs for QC standards all begin with the letter "F" due to the design of the NADP LIMS historically. See Acronym Table in **Appendix I** for a complete list of the QC acronyms. In the standard naming convention "L" is for low, "M" is for mid, "B" is for blank, and "FR50" is "faux rain" at approximately 50th percentile of historical field NTN concentrations. The FL, FB, FM, FR50 that are analyzed at the beginning of the run (after calibration) must meet acceptance criteria before sample analysis proceeds. The pH probe does not require an FB.

10.4.1 FL Standard (FL)

10.4.1.1 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. 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.

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

10.4.1.3 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 or qualified.

10.4.2 FR50 Standard

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

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

10.4.2.3 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

10.4.3.1 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.

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

10.4.3.3 FCRM Corrective Action: this is an ongoing QC tool and does <u>not</u> require immediate corrective action if control limits are exceeded. This is a tool used by the QA supervisor 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

10.4.4.1 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.

10.4.4.2 FMDL Monitoring Criteria: 70-130% recovery or +/- NTN MDL_N whichever is greater. Not analyzed for pH or conductivity.

10.4.4.3 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 supervisor 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 NTN and AMoN Batch QC Standards

10.5.1.1 Batch QC is analyzed within each analytical sequence (batch) at a frequency of after every 10 NTN or AMoN samples. All analytical QC failures are noted on data packets and also the possible qualifier log in LIMS if the sample cannot be successfully rerun.

10.5.2 FM Standard

10.5.2.1 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 or qualified if rerun is not possible.

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

10.5.2.3 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.

10.5.3 FB Standard

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

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

10.5.3.3 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.

10.5.4 Analytical Sample Duplicate

10.5.4.1 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.

10.5.4.2 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).

10.5.4.3 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.

10.5.4.4 If either the sample or duplicate fall in different result ranges (i.e. sample result is <MDL and duplicate result is MDL to 10x MDL) then the higher result range is used (for example given AD calculation would be used).

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

Sample Result	Duplicate Result	Calculation	Criteria
< MDL	< MDL	No Detect	None
MDL to 10 x MDL	MDL to 10 x MDL	Absolute Difference (AD)	+/- Network MDL
10 x MDL or greater	10 x MDL or greater	RPD	RPD within ±10%

10.6 NTN and AMoN Linear Dynamic Range and Carryover Determination

10.6.1 LDR

10.6.1.1 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.

10.6.1.2 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 the range from the MDL up to 20 mg/L for that analyte.

10.6.1.3 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 (i.e. within 20 mg/L from the above example).

10.6.1.4 If a non-diluted sample has a concentration greater than the LDR and there is enough sample remaining then two different dilution factors should be performed for comparison and the RPD between the two dilutions should be less than 10%.

10.6.1.5 If multiple samples in a batch are above the LDR, at least 10% of those samples require a dilution comparison.

10.6.1.6 The sample value would still be noted in the possible qualifiers table in LIMS, 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 due to unknown validity of the result.

10.6.2 Carryover

10.6.2.1 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.

10.6.2.2 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.

10.6.2.3 Application of Carryover: During an analytical run, if a sample value is greater than the determined carryover limit (i.e. 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 it cannot be rerun it will be listed in the potential qualifiers table in LIMs. Following the calculations in Table 4, duplicate calculations, will determine if carryover was present. If no carryover was present, the original value will be reported. If carryover is present, the rerun value will be reported. 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.

10.7 NTN and AMoN QC Rounding and Decimal Points

Table 5. NTN/AMoN QC Sample Results Assessment Rounding and Decimal Place Guidelines

Rounding Rule	If last number	Rounding Directions	QC Type	Decimal Place to Round to:
1	<5	Round Down	Blanks (FB) and Low (FL) Standards Results	3 decimal places (i.e. 0.234)
2	>5	Round Up	All other QC standard results	2 decimal places (i.e. 0.52)
3	= 5	If digit to the left of the 5 is even round down if it is odd round up	Percent recovery	Whole number (i.e. 98 %)

10.8 MDN Analytical QC

MDN QC samples are analyzed within each analytical sequence. See **Appendix G** for MDN 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.

10.8.1 Calibration Blanks (FCB)

10.8.1.1 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.

10.8.1.2 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.

10.8.1.3 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.

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

10.8.2.1 Calibration Description: A calibration is not required to be analyzed daily for mercury analysis. 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. 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.

10.8.2.2 Calibration Criteria: Each of the calibration standards must be recovered in the range of 85%-115% for total mercury per the reference method. These limits will be reassessed and possibly changed after enough QC data has been collected. The relative standard deviation of the calibration factors must be ≤15%.

10.8.2.3 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.

10.8.3 Continuing Calibration Blanks (FCCB)

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

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

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

10.8.4 Ongoing Precision and Recovery (FOPR)

10.8.4.1 FOPR Description: A calibration check at 5 ng/L for total 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.

10.8.4.2 FOPR Criterion: The FOPR must be recovered in the range of 80%-120% for total 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 THg.

10.8.4.3 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.

10.8.5 Ongoing Method Detection Limit Verification (FMDL)

10.8.5.1 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.

10.8.5.2 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.

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

10.9 MDN 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.

10.9.1 Digested Laboratory Reagent Blanks (FLRB)

10.9.1.1 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.

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

10.9.1.3 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 in LIMS for the data review staff.

10.9.2 Digested Quality Control Standard (FQCS)

10.9.2.1 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 treated with BrCl alongside the assigned sample batch.

10.9.2.2 FQCS Criterion: The FQCS must be recovered in the range of 80%-120% for total mercury.

10.9.2.3 FQCS Corrective Action: The run must be stopped and the issue assessed/resolved. If the system is cleaned 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.

10.9.3 Matrix Spikes and Matrix Spike Duplicates

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

10.9.3.2 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.

10.9.3.3 MS/MSD Criteria: The recovery of the spikes must be in the range of 75%-125% for total mercury. The absolute percent difference of the replicates (MS and MSD) must be ≤24% for total mercury. These limits are set by the reference method and will be reassessed when enough data has been accumulated.

10.9.3.4 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.

10.10 Uploading Analytical 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 or CLS Charts and Analysis. Calibration standards, failed NTN/AMoN duplicates/dilutions, and MDN MS/MSDs are not uploaded to LIMs. Instead, they are recorded in the data packets, the possible data qualifiers table in LIMS, 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 in the possible qualifiers table as well as on the relevant data packet. Duplicate failures are tracked on a shared spreadsheet which the QA staff reviews at least quarterly (O:\Teams\NADP\NADP Lab\QC failures\Duplicate Failures.xls).

10.11 PFN Analytical QC

10.11.1 Calibration

The LC-MS/MS instrument calibration is performed at least monthly and whenever a system change is made that affects sensitivity. On each analysis day a CCV is run and evaluated for accuracy before samples are analyzed. Seven non-zero standards (including all of the 40+ PFAS compounds) are analyzed for calibration and the curve fits may be linear or quadratic, as long as the correlation coefficient (r) is $\geq$0.995.

10.11.2 Calibration Verification

CCVs and CCBs are evaluated for every 10 samples. The initial CCV is evaluated in real-time before sample analysis can begin. Due to the complexity of analysis, number of compounds, and labor required for mass-spectral integration, all other QC evaluations are performed after the run is completed. Primary validation of the run is achieved by examination of the CCV and CCB controls. CCVs must recover between 70%-130% for each analyte in order to be accepted. CCBs must be below the MDL for each analyte. CCV and CCB results are uploaded to CLS. Failing CCV and CCB results will prompt a reanalysis, but are otherwise flagged.

10.11.3 Surrogates

Isotopically labeled surrogates are spiked into all calibrators, controls, and samples. The recovery of the surrogates in samples relative to the average surrogate response in the first two CCVs is used to calculate the analyte concentrations (i.e. an isotope dilution calculation). Surrogate recovery must be between 25-150% for most PFAS compounds and between 10-150% for neutral PFAS compounds. Surrogate recovery failures may prompt re-preparation of the sample if a systematic error is suspected, but are otherwise flagged.

10.11.4 Transition Ions

Transition ions are two or more fragments of the same precursor compound that are quantified in the mass-spectrometer and compared post-analysis. One fragment is the quantifier (used to calculate the analyte concentration), and additional fragments are qualifiers. The qualifier transition ion confirms both compound specificity and instrument performance. The transition ion ratio (TIR) for any

quantifier/qualifier pair must be between 50-150% if the quantifier is above the MDL. TIR is evaluated for all calibrators, controls, and samples. TIR failures may prompt reanalysis or repreparation, but are otherwise flagged.

10.11.5 Method Blanks

Method blanks are run and associated with each preparation batch. Any PFAS analytes in the method blank must be either <2x MDL or <5x the sample concentration for any sample/analyte in the batch to be accepted. Failures may prompt repreparation, but are otherwise flagged.

10.11.6 Laboratory Control Spikes

Laboratory control spikes are run and associated with each preparation batch to provide a metric of accuracy for each of the targeted PFAS analytes. Analytes must recover between 60-135% for any sample/analyte in the batch to be accepted. Failures may prompt repreparation, but are otherwise flagged.

10.11.7 Duplicates

Both procedural (full method, including the extraction step) and analytical duplicates (LC-MS/MS duplicates of prepared SPE extracts) are analyzed. Procedural duplicates are assigned at the time of sample login at a rate of 1 per 17 samples or fewer. Analytical duplicates are randomly selected at the time of analysis at a rate of 1 per 20 samples or fewer. For both types of duplicates, the RPD must be ≤30% for analytes that are at or above 2x the LOQ (also called MRL). For analyte concentrations between the MDL and 2x LOQ, the RPD must be ≤50%.

11. Method Detection Limits (MDLs)

Refer to **Appendix C** for the current and some historical MDLs. New MDLs are calculated each year and compared with previous years MDLs. MDLs will generally not be changed if the new MDL is within 0.5 – 2.0 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. Also reference MDL history in **Appendix C**.

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.

11.1.2 MDL_L Usage

The QA supervisor 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 lab supervisors and revised by the QA supervisor 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 supervisor 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.

11.2.2 Network MDL_N Usage

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 C**). 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. 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 and bolded if it is less than the NTN MDL_N for that calendar year. The Network MDL is also used to assess analytical QC results (i.e. continuing calibration blanks).

11.3 AMoN Lab MDL (MDL_L)

The AMoN lab MDL is now based on the average result for preparation blanks that had a measured value. This accounts for background contamination in the filters derived from the manufacturing process and the samplers during the cleaning and assembly.

11.3.1 AMoN MDL_L for data assessment

The AMoN Lab MDL (MDL_L) is used for bench level QC. 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 C** for a list of AMoN MDLs.

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. Each site receives at least 3 travel blanks per calendar year beginning in 2022. AMoN MDL_N = mean valid travel blanks + ($s * t^{99}$). See **Appendix C** for a list of AMoN MDLs.

11.4.2 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 F**). 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 supervisor 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 more frequent travel blanks or other

changes to the field QC may be instituted. There may be a need to flag potentially affected data 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 (triplicates no longer utilized), historically have not been flagged. The travel blanks will also be assessed quarterly and the criteria is that 90% of valid travel blank concentrations will be less than 0.1 mg/L NH_4. In addition, the travel blanks will be assessed by on a per site and seasonal basis to identify field related trends.

11.6 MDN MDLs

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.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. The MDN LOQ for total mercury is set to the lowest calibration standard.

11.6.1 MDN MDL Adjusted by Dilution

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

11.7 PFN MDL

11.7.1 PFN MDLs are calculated according to EHD QA 116 SOP and 40 CFR Part 136, **Appendix B**, using a minimum of 7 replicate spiked reagent solutions prepared in the laboratory and a minimum of 7 procedural blanks. MDLs are verified by analyzing a spiked solution, prepared at a concentration between 1-5x the initial MDL at a cadence of at least one preparation batch per month. Ongoing spiked and blank data are assessed annually. The PFN LOQs (or MRLs) are set to the lowest calibration standard (which is between 2-10x the MDL).

11.7.2 Because samples of varying initial volume can be SPE processed for PFAS analysis, but are all pre-concentrated to 1 mL, the MDL changes with the sample volume analyzed. The reference and standard volume is 250 mL, but may be increased or decreased depending on volume availability. A sample/analyte specific MDL is calculated by dividing the PFAS concentrations by the calculated concentration factor. The concentration factor is typically = 1mL/250 mL. This calculation is automated in the LIMS.

11.7.3 As of February 2026, PFN network MDLs have not yet been established. PFAS data acquired from NTN Network MDL samples are currently being collected to evaluate the need for a network MDL.

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 lab 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*** (2022). At the Fall 2021 NADP conference it was decided that the PO would be audited in 2022 and then in 2024 the lab and PO had a combined audit (after 3 years for lab but 2 for PO to get onto the same schedule) and then both will be audited every 3 years after that (i.e. joint review in 2027, 2030, 2033 etc.).

12.2 Internal Audits

Internal audits are conducted by the NADP QA staff. An internal systems audit will be done annually except on external audit years. The systems audit covers the overarching lab components outlined in this QAP. In addition, internal audits may be requested at any time by the NADP Management Team.

Method audits will be completed at a minimum of every two years for all NADP analytical methods except on external audit years. 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 supervisors are responsible for making sure corrective actions are implemented. The QA supervisor is responsible for retaining records of review findings, responses, and actions.

12.3 Proficiency Test Samples

Proficiency Test (PT) samples are prepared by an outside organization. The lab requests these samples to assess accuracy of analytical lab results. The vendors assemble the data from the participating laboratories and establish statistically determined consensus “true” concentration values against which each lab’s performance is judged. The lab is currently participating in two PT programs for NTN and MDN. There is also a USGS Interlaboratory Comparison program that the lab now participates in quarterly. PT results outside of the prescribed control limits will result in evaluation for corrective action and are reported on the WSLH Nonconformning Events Management System (see Section 13.6). The QA supervisor 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. USGS SRS and ECCC PTs (See Table 5) are transferred to 60 mL bottles and sent through the normal QC sample login process. The USGS Interlab PTs are single blind samples for the laboratory as their status, but not concentrations, as PT samples are known. The SRS/ECCC samples are double blind to the analysts whereby their PT status is masked. All NTN PT samples are analyzed in the same manner as network samples with the exception of filtration for NTN.

PFN will analyze drinking water PTs from ERA until another source is identified. NADP is working with USGS to establish a proficiency testing program for PFAS in precipitation.

Table 6. PT Providers

NADP PT Provider Information Updated 2/2026							
PT Provider	**Network**	**LAB ID**	**Study Timeframe**	**1st Enrolled**	**Name of PT**	**Analytes Available (Green we test)**	**Matrix**
Environment and Climate Change Canada	NTN and MDN	**F303**	Twice a Year - Spring and Fall	2018	RN - Rain and Soft Water	Acidity, alk, Al, NH3, Ca, Cl, Cond, C, F, Mg, Nitrate, pH, K, Na, SO4, TKN, TN	Natural Precip/Surface water
USGS PCQA Intercomparison	NTN	None	Quarterly Starting 2025	2018	USGS Intercomparison	NH4, Ca, Cl, Cond, Mg, Nitrate, pH, K, Na, SO4, OP	Natural filtered Precip
USGS PCQA Intercomparison	MDN	None	Quarterly Starting 2021	2019	USGS Intercomparison	Total Mercury - low level	Clean Spike
USGS SRS	NTN	**615**	Twice a Year - Spring and Fall	2021	USGS SRS NTN	Nutrients: Amm + OrgN as N, Ammonia as N, Nitrate as N, Nitrite + Nitrate as N, OrthoP as P, Total N as N, Total P as P Precip: Ca, Cl, Fluoride (F), Mg, OrthoP as P, pH, K, Na, Cond, SO4	Precip = Non preserved snowmelt, nutrients clean spike
USGS SRS	MDN	**615**	Twice a Year - Spring and Fall	2021	USGS SRS MDN	Total Mercury	Clean Spike
ERA	PFN	**N/A**	Twice a Year - Spring and Fall	Planned start of Spring 2026	ERA PFAS	PFAS Compounds	Clean Spike

ICAL ID WMO 70003, ECCC F053

USGS PT Website – https://www.usgs.gov/data/us-geological-survey-precipitation-chemistry-quality-assurance-project-data-2021-2022
USGS SRS Website – https://qsb.usgs.gov/srs/srs
WMO PT Website – http://qasac-americas.org/study-results

12.4 Nonconforming Event Management Reports

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

There are two lab-wide SOPs that document the use of Occurrence Management forms:
LABWIDE GENOP 711, Nonconforming Event Management Procedure for MediaLab
LABWIDE GENOP 707, Nonconforming Event Management System Policy

Whenever possible, supporting documentation is linked to the NCE form in the attachment tab.

Documentation of occurrences must be made either by the person who discovered the problem, their supervisor, or the QA supervisor. 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 NCE 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 supervisor and lab manager or supervisor. The lab manager or supervisor is responsible for management and evaluation of non-conforming work in consultation with the QA supervisor. The lab manager or supervisor 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 site 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 Nonconforming Event Management Reports (through MediaLab 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 Noncomforming Event 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 are 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 table in LIMs. See ***EHD NADP LAB QA/QC 202 - Peer Review of Analytical Process***.

13.1.1 Data packets for LC-MS/MS, CVAFS, ICP, FIA and IC must contain:

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

13.1.2 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 during analysis. 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. PFN sample and QC data are handled through CLS LIMS. Surrogate and TIR information are currently not uploaded. CLS performs volume preconcentration corrections and updates MDLs.

13.2.2 LIMS Compare Review

In addition to the peer review process, a randomly selected data packet for each platform is selected a minimum of once per quarter to do a 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 supervisor and/or lab supervisor 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 lab 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)
- 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 F** for Notes Codes Tables)

13.4 NTN and MDN Data Review Process Overview

13.4.1 NTN/MDN First Data Entry

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

13.4.2 NTN/MDN Second Data Entry

13.4.2.1 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

13.4.3.1 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

13.4.4.1 The 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 and 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/PFN Final Review

13.4.5.1 All sample related data are 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 and on the OneDrive (there is a log for AMoN, NTN, and MDN).

13.4.5.2 Sample Quality Rating (QR) codes are confirmed for validity.

13.4.5.3 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

13.4.6.1 Preliminary reports are sent to sites.

13.4.7 Published data

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

13.4.8 NOTE: PFN is a sub-network of NTN and relies on the NTN review process up to the point of concentration data transfer to the PO. Final review of concentration data for PFN is the responsibility of the PFAS laboratory staff, supervisor, and NADP Systems QA Manager.

13.5 AMoN Data Review Process Overview

13.5.1 AMoN First Data Entry

13.5.1.1 Lab receiving staff enters field form information into LIMS.

13.5.2 AMoN Review Report

13.5.2.1 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

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

13.5.4 AMoN Final Review

13.5.4.1 Chemistry results, address analytical notes, data flags (See **Appendix F**) 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

13.5.5.1 Preliminary reports are sent to sites.

13.5.6 Published data

13.5.6.1 Final data from the lab 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 H**)

14.1 Archive Software

In 2019, the lab instituted 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 lab is freezing all fixed and forever archive samples after a full tray has been shipped over from processing at AG. 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 (only fill to neck) to minimize bottle integrity issues from liquid expansion during freezing.

14.3 Archive Preservation Study

It is believed that the former lab 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 lab 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 lab 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 were quantified in this study and the data is currently being reviewed and written-up for publication in 2026.. The details of this study are in **Appendix H**.

14.4 AMoN Current Sample Archive

Excess AMoN extracts will be frozen in the original extraction tubes. The lab will utilize a 2-year AMoN extract retention period. If samples remain 3 months past the 3rd year anniversary. The lab discontinued the AMoN sample archive in early 2026 due to sample stability concerns and lack of archive requests.

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. At each fixed site a single monthly sample is randomly chosen (usually the first sample that month with

enough volume). Each monthly "fixed" sample will be archived (frozen) indefinitely. If all samples are dry for a month there will not be a fixed archive for that month. This differs from the "Forever" sites as all samples from those sites are saved, not just one per month.

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

The lab will at most keep the short-term sample archive for 5 years after login. Samples will be offered to the community before disposal. The lab 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 H** for table outlining the disposal schedule.

14.6 MDN Sample Archive

MDN samples are not archived.

14.7 MLN Sample Archive

MLN samples are archived at room temperature in their respective composite bag inside a bin. These samples are kept for 2 years on site.

14.8 PFAS Sample Archive

Because PFN is a sub-network of NTN, no additional archive is maintained. Secondary "backup" bottles of filtered samples with sufficient volumes are stored frozen at least until the data are released. However, PFN sample extracts (the 1.0 mL MeOH solutions) are being archived at -20C. These extracts can be used for re-analysis, quantification of new analytes as needed, and can be shared for interlaboratory comparisons. They may also be used for non-targeted PFAS efforts. While a disposal/storage time has not yet been established, we expect that it will be 5 years.

14.9 Disposal of NTN and AMoN samples

After archive periods have expired, precipitation samples and thawed AMoN abstracts are poured into a bucket or other large vessel and neutralized before pouring down the drain and the 60 mL bottles are recycled.

14.10 Disposal of MDN Samples

The bromine is neutralized with hydroxylamine hydrochloride, then the sample is dumped to sanitary sewer with excess tap water.

14.11 Disposal of MLN Samples

Litterfall samples may simply be discarded in a garbage receptacle.

14.12 Disposal of PFN Samples

These samples are not spiked with PFAS surrogates and may be disposed by draining to sanitary sewer.

14.13 Special Studies

The lab can provide in-coming (current) and/or archived (already processed and frozen) samples upon request from the National Trends Network (NTN) and archived samples for the Mercury Litterfall

Network (MLN). It is possible that MDN 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 lab managers and supervisors 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.

"Current" Samples (prior to archive)

1. **Unfiltered Sample** – Up to ~850 mL of NTN sample, available upon receipt of samples at the lab.
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 the lab 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 the lab. Additional volume could be filtered with possible extra cost.

Archive Samples (samples already processed and frozen)

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. MLN Archive Sample – composite available after data is published to the PO up to two years post collection season.

15. References

- EHD DIVISION-WIDE GENOP 029 – Data Integrity, Ethics, and Data Documentation Procedure
- EHD DIVISION-WIDE PLAN 001 – Quality Assurance Manual - General
- EHD NADP LAB GENOP 100 – Sample Log In and Data Entry
- EHD NADP LAB GENOP 405 – MDN Supply Prep
- EHD NADP LAB GENOP 411 – Preparation of Passive Ammonia Diffusive ALPHA Samplers
- EHD NADP LAB GENOP 412 – Extraction of Passive Ammonia Diffusive ALPHA Samplers
- EHD NADP LAB METHOD 502 – Determination of Ammonium by FIA
- EHD NADP LAB QA/QC 200 – NTN and MDN Supply Quality Control
- EHD NADP LAB QA/QC 202 – Peer Review of Analytical Process
- EHD NADP LAB QA/QC 204 – Pipette Verification
- EHD NADP LAB QA/QC 205 – Flask Verification
- EHD NADP LAB QA/QC 206 – Thermometer Verification
- EHD NADP PRC GENOP 001 – Testing Supplies, Reagents, and Equipment
- EHD NADP PRC METHOD 16001 – PFAS in Precipitation Low Volume
- LABWIDE GENOP 1002 – Records Storage and Disposal
- LABWIDE GENOP 1004 – Building Access Authorization
- LABWIDE GENOP 1101 – Visitor Access to WSLH Facilities
- LABWIDE GENOP 707 - Nonconforming Event Management System Policy
- LABWIDE GENOP 711 - Nonconforming Event Management Procedure for MediaLab
- LABWIDE SAFETY 101 – Emergency Response Plan for Agriculture Drive
- LABWIDE SAFETY 102 – Chemical Hygiene Plan and General Laboratory Safety Plan for Agriculture Drive
- LABWIDE SAFETY 201 – Emergency Response Plan for Henry Mall
- LABWIDE SAFETY 202 – Chemical Hygiene Plan and General Laboratory Safety Plan for Henry Mall
- LABWIDE SAFTEY 300 – WSLH Employee Safety Checklist
- NADP PO GENOP 001 - NADP Quality Management Plan

16. Version Tracking Table

Ver. #	Date	Changes Made	Author
Prior to OnBase 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
OB1	11/2021	Revised unique IDs, version numbers and SOP references for import to OnBase.	Nichole Davis
OB2	12/2021	Updated header – OB1 was mistakenly published without header update so had to go to OB2	Camille Danielson
OB3	3/2022	• Removed most references to CAL and HAL – instead differentiate by networks • Added Litterfall Network (MLN) • Added information on new SOP module – OnBase • Clarified AMoN Prep DOC • Added QA and You and OnBase training • Added thermometer verification information • Added syringe QC • Removed requirement for acid bath testing • Updated network qualifiers table • Changed NTN archiving procedure to use the analytical bottle • Updated Field deployment, field and lab hold times for all networks	Camille Danielson

		• Removed reference to high and low level ICP calibrations • Simplified the analytical Duplicate table • Clarified LDR procedure • Added NTN and AMoN QC result rounding and decimal place guidelines • Updated MDLs for 2021 and 2022 • Adjusted AMoN Field QC to minimum of 3 duplicate sets and 3 travel blanks per site per year • Changed external audit schedule to be combined with PO every 3 years after 2024 combined audit • Changed internal lab systems audit to be every year there is not an external audit • Added sample disposal information • Moved MDL detailed information to the appendix • Added a table for rounding rules • Changed balance and weight certification timeframes • Updated PT/SRS information • Updated Org Charts, MDL Tables, QC supply tables and notes codes • Added Approval Table to record external approvals	
OB4	4/2023	• Updated title changes throughout the lab • Updated references of the possible data qualifiers from the spreadsheet to LIMS table • Updated Table 1 – NADP Network Summary • Updated Table 3 – NTN Volume Assessment • Updated Org Charts, MDL tables, QC supply and frequency tables, AMoN Preparation QC table, and NTN/AMoN Control Limits table	Nichole Miller
OB5	3/2025	• Update the new nomenclature of NAL where needed • Updated title changes throughout the lab • Updated operation locations where needed with probes at AG • Updated the use of Canvas for annual readings • Added volumetric flask verification process • Removed methyl mercury analytical detials • Updated the NCEM software from Footprints to MediaLab • Updated out of date tables and figures in the appendicies • Updated the index	Nichole Miller

OB6	2/2026	• Added information for each section related to the PFAS sub-network • Updated references from Radiellos to ALPHAs • Updated the PT section since WMO has stopped • Removed AMoN and added MLN to archive requests • Updated any tables and figures that were outdated • Added a reference section • Updated the index	Christa Dahman, Martin Shafer, Nichole Miller, Sarah Benish

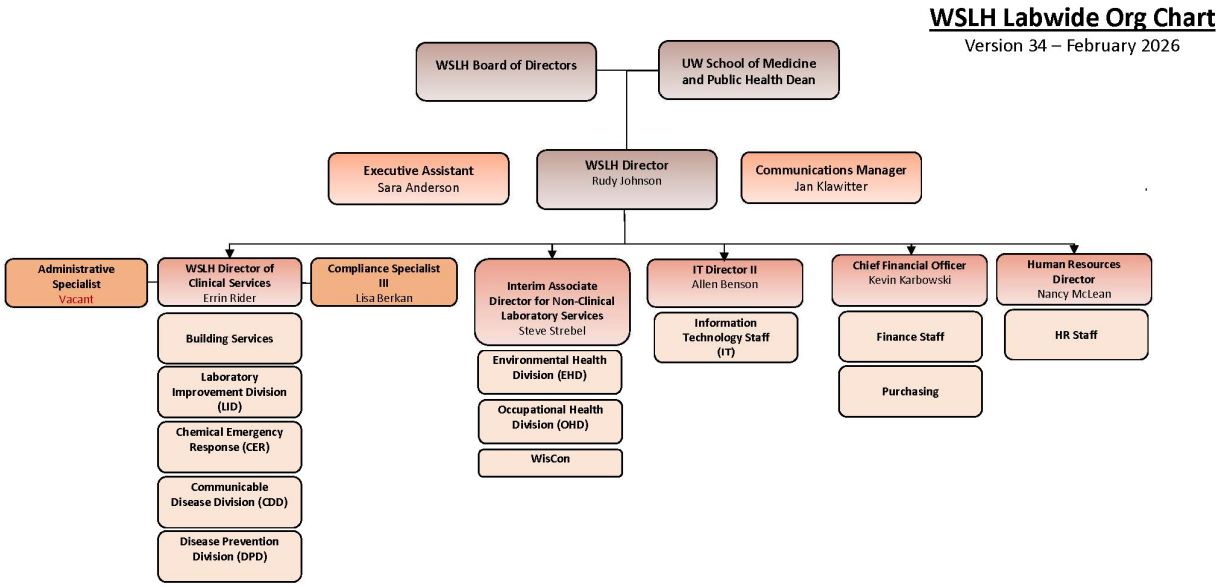
17. Approval Tracking Table

Version	Representing	Changes Approved by:	Date Approved
OB Version 6	NADP Lab	Nichole Miller	2/21/2026
OB Version 6	NADP PO	Sarah Benish approved edits	2/23/2026
OB Version 6	QAAG	QAAG Members approved edited version via Qualtrics survey	3/2/2026

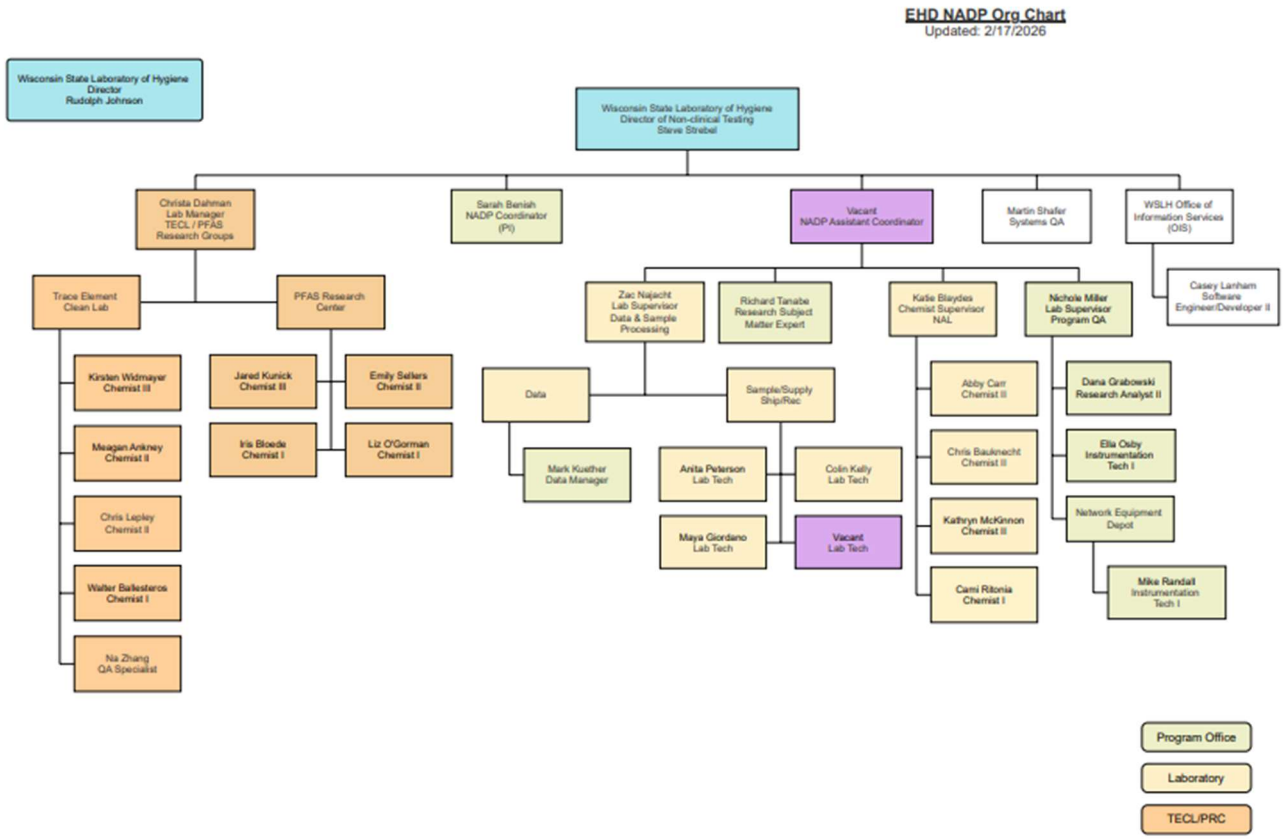
18. NADP Lab QAP Appendices

Appendix A. WSLH Organizational Charts

Appendix A1. WSLH Labwide Organizational Chart



Appendix A2. EHD – NADP Organizational Chart



Appendix B. 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
Cold Vapor Atomic Fluorescence Spectrometer	Total Mercury	Hg	Tekran 2600
Atomic Absorption Spectrophotometer	Mercury in solids	Hg	Nippon MA3000
Liquid Chromatography Tandem Mass Spectrometry (LC-MS/MS)	PFAS	See analytical SOP	AB SCIEX Q-Trap 7500
PFAS Solid Phase Extraction	PFAS	See analytical SOP	Promochrom Automated Extractor

Appendix C. Detection Limits

Appendix C1. NTN Current Method Detection Limits 2025

2025 NADP Lab/Network NTN MDLs mg/L				Version 2/18/2025					
NTN	Ca^{2+}	Na^{+}	K^{+}	Mg^{2+}	Cl^{-}	$SO4^{2-}$	NO_3^{-}	NH_4^{+}	PO_4^{3-}
LAB MDL MDL_L	0.003	0.007	0.009	0.001	0.013	0.011	0.008	0.009	0.013
NETWORK MDL (MDL_N)*	0.008	0.008	0.006	0.004	0.020	0.020	0.020	0.014	0.010

**Network MDL used at the bench and for censoring NTN data less than MDL_N. Lab MDL indicates analytical capability.*

Appendix C2. AMoN Detection Limits

AMoN Sample Set ID Range	Year of Sample Receipt	AMoN Network MDL (MDL_N) mg/L NH_4^{+}	AMoN Lab MDL (MDL_L) mg/L NH_4^{+}
All Prior to N18005002	<2018	0.0469	0.0469
N18005002 - N18006407	2018	0.119	0.008
N19000001 - N19002669	2019	0.104	0.016
N20000001 - N20002856	2020	0.083	0.013
N21000001 - N21003101	2021	0.070	0.010
N22000000 - N22002743	2022	0.080	0.010
N23000001 - N23002490	2023	0.084	0.014
N24000001 - N24002468	2024	0.084	0.014
N25000001 - N25002695	2025	0.084	0.014
N26000001-ongoing	2026	0.030	0.030
		Used to flag samplers < as "d"	*Used at bench and to flag only TBs < as "d"*

Appendix C3. MDN Detection Limits

MDN MDLs	Limit of Detection as Mass (pg)	Standard Sample Volume (mL)	Lab Detection Limit (ng/L)	Limit of Quantitation (ng/L)
Total Hg MDL_L	6	30	**0.200**	**0.500**
Total Hg MDL_N			**0.098**	

Appendix C4. PFN Detection Limits

			As-analyzed		250mL sample	
Analyte	**Abbreviation**	**CAS No.**	**MDL (ng/mL)**	**MRL (ng/mL)**	**MDL (ng/L)**	**MRL (ng/L)**
Perfluoro-n-butanoic acid	PFBA	375-22-4	0.0267	0.05	0.1068	0.2
Perfluoro-n-pentanoic acid	PFPeA	2706-90-3	0.00997	0.025	0.0399	0.1
Perfluoro-1-butanesulfonate	PFBS	375-73-5	0.01008	0.0221	0.0403	0.0885
1H,1H,2H,2H-Perfluorohexane sulphonic acid	4:2 FTS	757124-72-4	0.01178	0.0235	0.0471	0.0938
Perfluoro-n-hexanoic acid	PFHxA	307-24-4	0.00941	0.025	0.0376	0.1
Perfluoro-1-pentanesulfonate	PFPeS	2706-91-4	0.00904	0.0235	0.0362	0.094
2,3,3,3-Tetrafluoro-2-(1,1,2,2,3,3-heptafluoropropoxy)-propanoic acid	HFPO-DA	13252-13-6	0.01353	0.025	0.0541	0.1
Perfluoro-n-heptanoic acid	PFHpA	375-85-9	0.01121	0.025	0.0448	0.1
Perflioro-1-hexanesulfonate	PFHxS	355-46-4	0.00874	0.0228	0.035	0.0913
Dodecafluoro-3H-4,8-dioxanoanoate	DONA	919005-14-4	0.0175	0.0473	0.07	0.189
1H,1H,2H,2H-Tridecafluorooctane-1-sulphonic acid	6:2 FTS	27619-97-2	0.01152	0.0238	0.0461	0.0952
Perfluoro-n-octanoic acid	PFOA	335-67-1	0.01325	0.025	0.053	0.1
Perfluoro-1-heptanesulfonate	PFHpS	375-92-8	0.00866	0.0239	0.0347	0.0954
Perfluoro-1-octanesulfonate	PFOS	1763-23-1	0.01002	0.0232	0.0401	0.0926
Perfluoro-n-nonanoic acid	PFNA	375-95-1	0.0075	0.025	0.03	0.1
Potassium 9-chlorohexadecafluoro-3-oxanonane-1-sulfonate	9Cl-PF3ONS	756426-58-1	0.00767	0.0234	0.0307	0.0935
1H,1H,2H,2H-Perfluorodecanesulphonic acid	8:2 FTS	39108-34-4	0.01284	0.024	0.0514	0.096
Perfluoro-n-decanoic acid	PFDA	335-76-2	0.014	0.025	0.056	0.1
Perfluoro-1-nonanesulfonate	PFNS	68259-12-1	0.00694	0.0241	0.0277	0.0962
N-methyl perfluorooctanesulfonamidoacetic acid	N-MeFOSAA	2355-31-9	0.01049	0.025	0.042	0.1
N-ethyl perfluorooctanesulfonamidoacetic acid	N-EtFOSAA	2991-50-6	0.01423	0.025	0.0569	0.1
Perfluorooctanesulphonamide	FOSA	754-91-6	0.00781	0.025	0.0312	0.1
Perfluoro-n-undecanoic acid	PFUnA	2058-94-8	0.01265	0.025	0.0506	0.1
Perfluoro-1-decanesulfonate	PFDS	335-77-3	0.00902	0.0241	0.0361	0.0964
Potassium 11-chloroeicosafluoro-3-oxaundecane-1-sulfonate	11Cl-PF3OUdS	763051-92-9	0.00854	0.0236	0.0341	0.0945
Perfluoro-n-dodecanoic acid	PFDoA	307-55-1	0.01272	0.025	0.0509	0.1
Perfluoro-1-dodecanesulfonate	PFDoS	79780-39-5	0.00818	0.0243	0.0327	0.097

Perfluoro-n-tridecanoic acid	PFTrDA	72629-94-8	0.01822	0.050	0.0729	0.2
N-Methyl Perfluorooctanesulfonamide	N-MeFOSA	31506-32-8	0.00845	0.025	0.0338	0.1
2-(N-methylperfluoro-1-octanesulfonamido)-ethanol	N-MeFOSE	24448-09-7	0.01066	0.025	0.0426	0.1
N-Ethyl Perfluorooctanesulfonamide	N-EtFOSA	4151-50-2	0.0079	0.025	0.0316	0.1
2-(N-ethylperfluoro-1-octanesulfonamido)-ethanol	N-EtFOSE	1691-99-2	0.01591	0.025	0.0637	0.1
Perfluoro-n-tetradecanoic acid	PFTeDA	376-06-7	0.0147	0.025	0.0588	0.1
Perfluoro-4-oxapentanoic acid	PFMPA	377-73-1	0.0109	0.025	0.0436	0.10
Perfluoro-5-oxahexanoic acid	PFMBA	863090-89-5	0.00942	0.025	0.0377	0.1
Perfluoro-3,6-dioxaheptanoic acid	NFDHA	151772-58-6	0.03679	0.100	0.1472	0.4
Potassium perfluoro(2-ethoxyethane)sulfonate	PFEESA	113507-82-7	0.01476	0.0223	0.0591	0.089
3-Perfluoropropyl propanoic acid	3:3 FTCA	356-02-5	0.01267	0.020	0.0507	0.08
3-Perfluoropentyl propanoic acid	5:3 FTCA	811-572-3	0.03465	0.100	0.1386	0.4
3-Perfluoroheptyl propanoic acid	7:3 FTCA	812-70-4	0.11653	0.250	0.4661	1.0

Appendix C5. NTN Historical Network Detection Limits

NTN Historical Network Method Detection Limits (mg/L) Revision 2/2026

Sample Start ID	Sample End ID	Aproximate Year RCV	Ca	Na	K	Mg	Cl	SO4	NO3	NH4	PO4	Br
NA0001	NA0067	1978	0.010	0.004	0.002	0.002	0.050	0.010	0.030	0.030	0.005	NA
NA0068	NA0104	1978	0.010	0.004	0.002	0.002	0.050	0.010	0.030	0.030	0.004	NA
NA0105	NA0221	1978	0.010	0.004	0.002	0.002	0.050	0.010	0.030	0.020	0.004	NA
NA0222	NA0335	1978	0.020	0.004	0.002	0.002	0.050	0.010	0.030	0.020	0.004	NA
NA0336	NA0446	1978	0.010	0.004	0.004	0.002	0.050	0.010	0.030	0.020	0.004	NA
NA0447	NA0452	1978	0.010	0.004	0.002	0.002	0.050	0.010	0.030	0.020	0.004	NA
NA0453	NA0668	1978	0.010	0.004	0.002	0.002	0.050	0.010	0.030	0.020	0.003	NA
NA0669	NA1331	1979	0.020	0.004	0.002	0.002	0.050	0.010	0.030	0.020	0.003	NA
NA1332	NA1675	1979	0.020	0.004	0.004	0.002	0.050	0.010	0.030	0.020	0.003	NA
NA1676	NA1800	1979	0.020	0.004	0.002	0.002	0.050	0.010	0.030	0.020	0.003	NA
NA1801	NA3361	1980	0.020	0.004	0.004	0.002	0.050	0.010	0.030	0.020	0.003	NA
NA3362	NA3475	1980	0.008	0.004	0.004	0.002	0.050	0.010	0.030	0.020	0.003	NA
NA3476	NA3695	1980	0.008	0.002	0.002	0.002	0.050	0.010	0.030	0.020	0.003	NA
NA3696	NA4254	1980	0.006	0.002	0.002	0.002	0.050	0.010	0.030	0.020	0.003	NA
NA4255	NA6000	1981	0.008	0.002	0.002	0.002	0.050	0.010	0.030	0.020	0.003	NA
NA6001	NA6328	1981	0.008	0.002	0.003	0.002	0.020	0.010	0.030	0.010	0.003	NA
NA6329	NA6543	1981	0.024	0.002	0.003	0.009	0.020	0.010	0.030	0.010	0.003	NA

NA6544	NA6650	1981	0.009	0.002	0.003	0.002	0.020	0.010	0.030	0.010	0.003	NA
NA6651	NA7299	1981	0.009	0.002	0.003	0.002	0.020	0.010	0.030	0.020	0.003	NA
NA7300	NA7741	1981	0.009	0.002	0.003	0.003	0.020	0.010	0.030	0.020	0.003	NA
NA7742	ND1937	1981-1985	0.009	0.003	0.003	0.003	0.020	0.010	0.030	0.020	0.003	NA
ND1938	ND1938	1985	0.009	0.003	0.003	0.003	0.030	0.010	0.030	0.020	0.003	NA
ND1939	ND2633	1985	0.009	0.003	0.003	0.003	0.030	0.030	0.030	0.020	0.003	NA
ND2634	NF4630	1985-1987	0.009	0.003	0.003	0.003	0.030	0.030	0.030	0.020	0.010	NA
NF4631	NH6700	1987-1989	0.009	0.003	0.003	0.003	0.030	0.030	0.030	0.020	0.020	NA
NH6701	NM6824	1989-1993	0.009	0.003	0.003	0.003	0.030	0.030	0.030	0.020	0.020	NA
NM6825	NS3700	1993-1998	0.009	0.003	0.003	0.003	0.030	0.030	0.030	0.020	0.003	NA
NS3701	NU7200	1998-2000	0.009	0.003	0.003	0.003	0.005	0.010	0.010	0.020	0.003	NA
NU7201	NW0218	2000-2001	0.009	0.003	0.003	0.003	0.005	0.010	0.010	0.020	0.009	NA
NW0219	NZ9957	2001-2004	0.009	0.003	0.003	0.003	0.005	0.010	0.010	0.020	0.006	NA
NZ9958	TA0214	2004	0.009	0.003	0.003	0.003	0.008	0.013	0.009	0.020	0.006	NA
TA0215	TA0334	2004	0.002	0.003	0.001	0.001	0.008	0.013	0.009	0.020	0.006	NA
TA0335	TB4169	2005	0.002	0.003	0.001	0.001	0.008	0.013	0.009	0.005	0.006	NA
TB4170	TE3724	2006-2007	0.002	0.001	0.001	0.001	0.003	0.010	0.017	0.004	0.004	NA
TE3725	TG9571	2007-2009	0.006	0.001	0.001	0.001	0.004	0.010	0.009	0.006	0.004	NA
TG9572	TI2460	2009-2010	0.004	0.003	0.001	0.001	0.003	0.004	0.005	0.010	0.008	NA
TJ5599	TM2704	2011-2013	0.005	0.002	0.003	0.002	0.009	0.010	0.010	0.009	0.005	0.005
TM2705	TN2615	2014	0.019	0.005	0.001	0.005	0.008	0.005	0.007	0.017	0.009	0.005
TN2616	TP0369	2015	0.009	0.006	0.002	0.002	0.005	0.005	0.005	0.016	0.005	0.005
TP0370	TQ4360	2016	0.009	0.003	0.004	0.002	0.005	0.004	0.005	0.019	0.005	0.004
TQ4361	TS9999	2017	0.006	0.002	0.002	0.002	0.003	0.005	0.005	0.018	0.006	0.004
TT0001	TT7317	2018	0.011	0.004	0.005	0.003	0.006	0.007	0.008	0.008	0.008	0.006
TT7318	TV0257	2019	0.023	0.010	0.005	0.006	0.018	0.018	0.018	0.017	0.010	0.006
TV0258	TW3112	2020	0.023	0.01	0.005	0.006	0.018	0.018	0.018	0.017	0.010	0.006
TW3113	TX6193	2021	0.010	0.008	0.006	0.006	0.020	0.020	0.020	0.014	0.010	NA
TX6194	TY9103	2022	0.010	0.008	0.006	0.004	0.020	0.020	0.020	0.014	0.010	NA
TY9104	UA1999	2023	0.008	0.008	0.006	0.004	0.020	0.020	0.020	0.014	0.010	NA
UA2000	T2410258	2024	0.008	0.008	0.006	0.004	0.020	0.020	0.020	0.014	0.010	NA
T2500001	T2511772	2025	0.008	0.008	0.006	0.004	0.020	0.020	0.020	0.014	0.010	NA
T2600001	Ongoing	2026	0.008	0.008	0.006	0.004	0.020	0.020	0.020	0.014	0.010	NA

*Naming sequence changed in March 2024 to better align with other networks format.

Appendix C6. MDL History Calculation Detials

NTN Laboratory MDLs

NTN 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 Appendix B to 40 CFR part 136 is calculated as sample standard deviation * the Student's t statistic at 99% confidence level. All valid MDL solution 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.

NTN 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 replace previous analytical lab MDL if the result is greater than the spiked lab MDL result and is within 0.5 to 2.0 times the previous analytical MDL. 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.

NTN Network MDLs

NTN 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. More recently, just Type I water has been put through the MDL process. 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/bag exposure, filtering and transferring to bottles) and are blind to the bench chemists that analyze them. 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 lined with a

new NTN bag, covered with a clean lid and left in the lab at least overnight. The next day the solution is poured into a 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 within 0.5 to 2.0 times the previous year, the lab may choose to keep the MDL values the same for another year.

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. MDLs based on buckets for 2019 were applied to 2020 data.

The 2021 MDLs were calculated by assessing the method blanks as well as processed blanks. The network maximum contamination level and the level of data that would be censored by increasing MDLs was also taken into consideration. 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. 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 was 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 and bolded if it is less than the NTN MDL_N for that calendar year. The Network MDL is also used to assess analytical QC results (i.e. continuing calibration blanks).

AMoN Lab MDL (MDL_L)

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. In 2021, the AMoN lab MDL was based on the average result for core blanks that had a measured value of 0.000 or greater (negative values removed). This result was confirmed with calculations in 2022 and will remain the same. 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.

AMoN Network MDLs

AMoN MDL_N Calculations

The network specific AMoN method detection limit (AMoN MDL_N) will be calculated annually from valid travel blanks. 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. Each sites receive at least 3 travel blanks per calendar year beginning in 2022. Before 2022, approximately 25% of sites received travel blanks on a rotating basis with each bimonthly deployment. In 2021 this equated to over 500 valid travel blank data points. 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 + ($s * t^{99}$).

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 MDLN 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.

AMoN MDL_N 2021 - 2022

The 2021 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 2021 MDL_N was calculated from 523 valid travel blanks with "end dates" (end of deployment period) from January 2021 to November 2021. The network MDL for 2021 deployed samplers is 0.070 mg/L NH_4. This result was recalculated in 2022 and yielded a network MDL of 0.080 mg/L NH_4 for samples received in 2022.

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 F**). AMoN data is reported with a QR code and is not "censored" to the MDL_N.

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 more frequent travel blanks or other changes to the field QC may be instituted. There may be a need to flag potentially affected data 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. The travel blanks will also be assessed quarterly and the criteria is that 90% of valid travel blank concentrations will be less than 0.1 mg/L NH_4. In addition, the travel blanks will be assessed on a per site and seasonal basis to identify field related trends.

MDN MDLs

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

MDN MDL Establishment

Initially, a minimum of seven method blanks and seven spiked samples are prepared and analyzed over three different analytical batches. 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 critical value at the 99th percentile (per Appendix B to 40 CFR part 136 federal

regulations). The MDL of the blanks is calculated by multiplying the standard deviation of the measured concentrations of the blanks samples by the students' t critical 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.

Ongoing MDN MDLs

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. The MDN LOQ for total mercury is set to the lowest calibration standard.

MDN MDL Adjusted by Dilution

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.

Appendix D. Supply QC

Appendix D1. Supply Lot Approval QC Log In and Frequency for NTN and MDN

NADP NTN and MDN Supply Lot Approval QC Frequency and Log In (Version 6 (2024) 6/12/2024)

Item	Solution	Amount & Frequency	Project	Client Number*	LIMS Description	Rinse Collection Bottle?**
BAG LOTS						
NTN Sample Bags	~150 mL MQ/~250 Spike	15/new lot (unless <2000 then 10)	New Sampling Bag Lot Check	Date Collected & Collector Initials	Bag Type, Lot #, Bag# (i.e. NTN Sample Bag Lot X 1of20)	Yes
NTN Bucket or Lid Bags	~150 mL MQ	5/new lot	Bag Blank Study	Date Collected & Collector Initials	Bag Type, Lot #, Bag# (i.e. NTN Bucket Bag Lot X 1of5)	Yes
BOTTLE LOTS						
NTN 60mL HDPE Bottles	~60mL MQ	10/new lot (unless <100 then 5)	NADP New Bottle Blanks	Date Collected & Collector Initials	Bottle Type, Lot #, Bottle# (i.e. 60mL NTN LotX 1of10)	No
NTN 1 Liter HDPE (New)	~150 mL MQ	10/new lot (unless <100 then 5)	NADP New Bottle Blanks	Date Collected & Collector Initials	Bottle Type, Lot #, Bottle# (i.e. 1L NTN LotX 1of10)	No
MDN PETG or PET 125 mL, 250 mL, 1L or 2L	20 mL 1% HCl + 100mL MQ	20/new lot from 10 boxes (unless <200 then 2%)	MDN Bottle Blanks	Date Collected & Collector Initials	Bottle Type, Lot #, BottleID, Bottle# (i.e. 250mL MDN LotX; 1of10)	No
FILTER LOTS						
NTN 47mm Disc Filters	60 mL MQ	20/New Lot min 2 boxes from lot	Filter Blank Lot Testing	Date Collected & Collector Initials	Lot, Box#, Filter #, Brand, filter type	Yes
NTN Syringe Filters	20 mL MQ	5 per lot of 150	Filter Blank Lot Testing	Date Collected & Collector Initials	Lot, Box#, Filter #, Brand, filter type	Yes
NTN Syringes	20 mL MQ	5 per lot of 150	Filter Blank Lot Testing	Date Collected & Collector Initials	Lot of Syringes, Syringe number	Yes
TUBE LOTS						
NTN Test Tubes	2-10 mL MQ	10/New Lot ICP/FIA	Test Tube QC Blank	Date Collected & Collector Initials	Brand, Test tube type, lot # & tube # (i.e. Fisher, ICP, Lot 3434, 2 of 10)	No
OTHER LOTS						
MDN Acid Preservative	30 mL (15 mL analyzed)	2/Batch of Acid Preservative with 1 lot	Acid Checks	Date Collected & Collector Initials	"Acid Preservative Blank", Acid Lot # and Batch ID	Yes
Must Meet LOT Approval Before Use of these Supplies						

Appendix D2. Ongoing Supply QC Log In and Frequency for NTN and MDN

NADP NTN and MDN Ongoing Supply QC Frequency/Log In (Version 5 (2024) 6/12/2024)

Item	Project	Amount/Frequency	Solution	Rinse Collection Bottle?**	Client Number*	LIMS Description
NTN SUPPLIES						
NTN 60 mL bottes	Bottle Blanks	2 bottles per month	60 mL MQ	No	Date Collected & Collector Initials	"Ongoing 60 mL from bin LOT#"
NTN 47mm Disc Filters	Filter Blanks DI	1/ Filter day	60 mL MQ	Yes	Date Collected & Collector Initials	"Start OR End Filter" & Sample Range
NTN Syringe Filters	Weekly Syringe Filter Blank	1 per month	20 mL MQ	Yes	Date Collected & Collector Initials	"Syringe Filter Blank", Syringe and Filter Lot#
NTN Sample Bags	Bag Blank Study	2/month	~150 mL MQ	Yes	Date Collected & Collector Initials	Bag Type, Lot#
NTN 1 Liter HDPE	Bottle Blanks	1/wash day	~150 mL MQ	Yes	Date Collected & Collector Initials	"1L NTN Washed"
NTN Buckets	Bucket Blanks	1/wash day	~150 mL MQ	Yes	Date Collected & Collector Initials	"New" or "Used" "Bucket"
NTN Lids	Lid Blanks	1/wash day /per type	~100 mL MQ	Yes	Date Collected & Collector Initials	Lid Type
MDN SUPPLIES						
MDN Sample Train	Sample Train Blanks	1/week in bag ≥2 days	~ 100 mL MQ	No	Date Collected & Collector Initials	"Sample Train Week of XXXXX"
MDN Travel Blanks	MDN Travel Blanks	Up to 4 a month	acid preservation in bottle	No	Date Collected & Collector Initials	Site ID shipped from, approximate time in the field (i.e. 4 weeks)
QC STANDARDS						
NTN MDL Sample	NTN MDL Sample	2 times per month	150 mL MDL sol. or Type I	No	Date Collected & Collector Initials	NADP MDL Solution ID (or Type I Water), Bag Lot if new
Special Checks	**Special QA Checks**	As needed	Varies	**Varies**	Date Collected & Collector Initials	Test Info

Appendix D3. Supply QC Log In and Frequency for AMoN

NADP AMoN Supply QC Frequency and QC Log In to LIMS (Version 6 (2026) 2/12/2026)

Item	Solution	Amount & Frequency	Project	Client Number	LIMS Description
Blanks With Cores					
Filter Blanks	10 mL MQ	10 per NEW lot **only for new lots on arrival**	**AMoN QA Samples**	Date Extracted and Initials	**"Filter Blank" and Filter lot**
Prep Blanks (fully assembled body)	10 mL MQ	2/sampler prep batch per sonicator	**AMoN QA Samples**	Date Extracted and Initials	**"Preparation Blank", Sampler batch ID, and Core lot**
Water Only Blanks					
Source Blank	10 mL Sonicator Source H_2O	1/sampler wash batch day	**AMoN QA Samples**	Date Prepped and Initials	**"Source Blank", Sampler batch**
Method Blank (extraction water)	10 mL MQ	1/extraction day	**AMoN QA Samples**	Date Prepped and Initials	**"Method Blank", water source - (from dispenser)**
Hood/Room Blanks					
2 Week Blank Sonicator Hood	10 mL MQ	1/two week period	**AMoN QA Samples**	Date Extracted and Initials	**"AIR Sonic Hood", Deployment Minutes**
2 Week Blank Extraction Hood	10 mL MQ	1/two week period	**AMoN QA Samples**	Date Extracted and Initials	**"AIR Extraction Hood", Deployment minutes**

Appendix D4. AMoN Preparation QC Criteria

NADP Lab AMoN Preparation QC Sample Control Limits (Revision 2/18/2026)

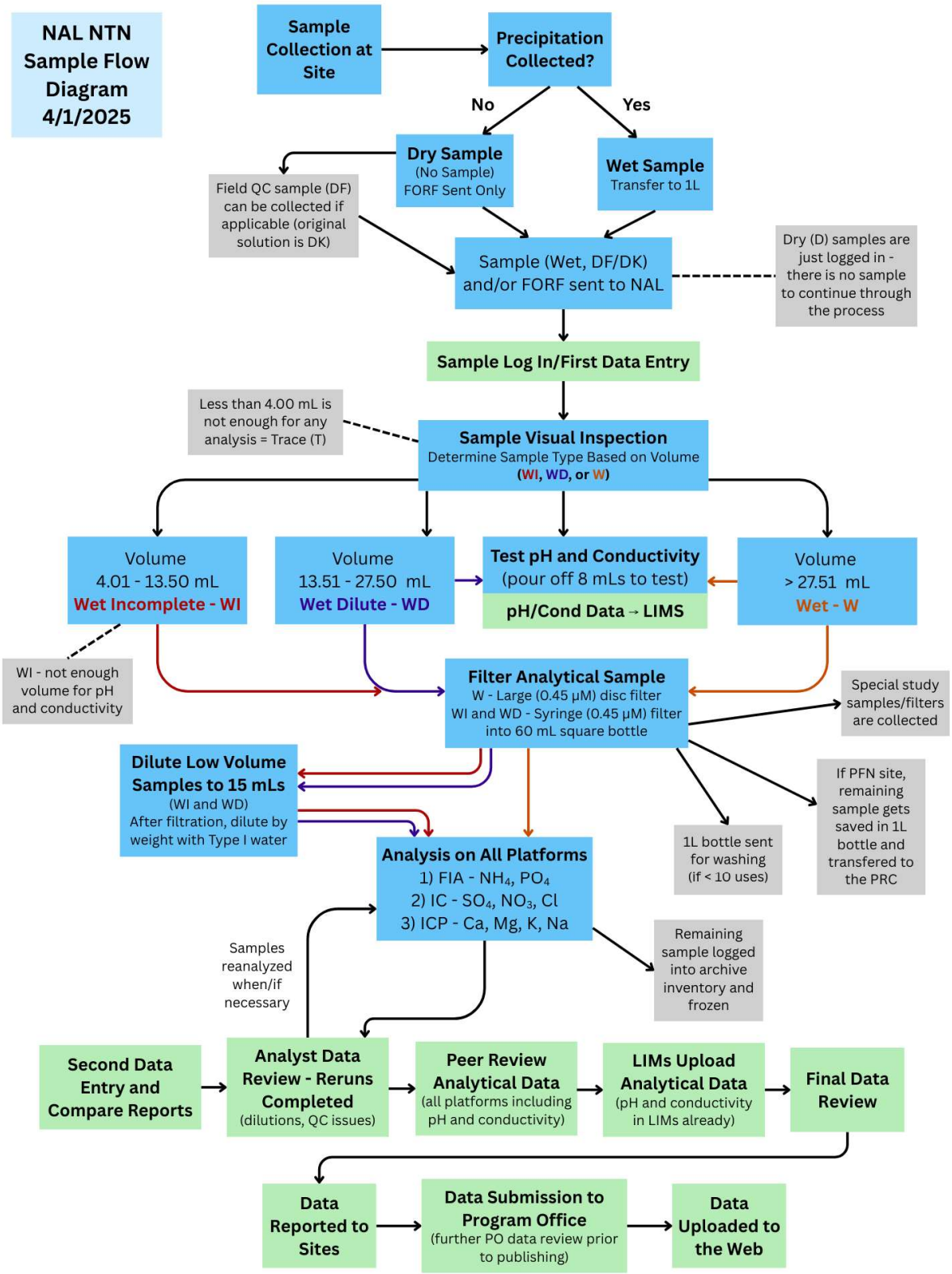
QC Type	Description	Frequency	Criterion	Origin of Criterion	Corrective Action
Preparation Blank	Fully Assembled sampler, frozen at least one night before extraction	2 per sampler preparation batch (each assembly day is 1 batch)	**<0.030 mg/L NH_4^+**	Less than mean travel blank level 2025	Determine if whole batch or a core lot issue by testing more cores. If extreme exceedance re-clean samplers in batch and/or replace cores and retest. Or add qualifier to samplers (q flag=QRB).
Filter Blank	Brand new core extracted without acidification	10 per new lot	**<0.018 mg/L NH_4^+**	Less than mean filter blank level 2025	Assess scope of issue. Action can include: test 3 more cores from lot, pull lot from use, return core lot, qualify data from batch of samplers if cores used (q flag=QRB).
Method Blank	Type I water from the auto dispenser used for extractions	1 per extraction day	**< 0.030 mg/L NH_4^+**	Analytical NH_4 $MDL_{L\ 2025}$	Compare to samplers/QC from same extraction. Samples associated with blank must be qualified due to possible contamination (qflag=QR B).
Source Blank	Water source for sonicators used during cleaning process	1 per prep batch	**< 0.030 mg/L NH_4^+**	Analytical NH_4 $MDL_{L\ 2023}$	Use w/other QC samples to determine root cause. Indicates potential issue with cleaning. CA includes: cleaning of sonicator baths, baskets, and covers, test Type I water, check solutions.
Hood - 2 Week Blank	Sampler deployed in hoods for two week period	1 per two week period per hood (adjusted to 2 weeks)	**< 0.400 mg/L NH_4^+**	2 X the travel blank criteria	Review QC samples from same time for correlation w/higher blank values. Check for power failures or other issues (filters) with hoods. Deploy room blank if failures.
Travel Blanks	Fully prepared sampler sent along with sampler to be deployed	~10% of sites receive travel blanks/deployment	**< 0.200 mg/L NH_4^+**	Historical NADP TB Criteria	Check 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) not flagged. Check Body IDs for length of use.
Field Duplicates	2 samplers sent to site for deployment (may incorporate new sampler body in duplicate sets to ID body age issue)	~10% of sites receive duplicates/deployment	**AD of < 0.1 mg/L NH_4^+**	Difference > 99th % TB	Duplicate results > 10 X MDL_N with > 15% RPD should be reanalyzed. Body IDs checked age/# of uses as possible cause (permeability/cleanliness). Both sampler results flagged (qflag).

Appendix D5. PFN Supply Lot Approval QC for PFN

Item	Solution	Amount & Frequency	Client	Profile	Additional Information Recorded in LIMS
HDPE bottles (250 mL, 1000 mL)	Fill with water; prepare as method blank	3 per lot (no ongoing testing)	LH054	PFAS QC	Lot, preparation reagents/volumes, date
Conical centrifuge tubes (15, 50 mL)	Methanolic ammonium hydroxide, ~1/2 full	3 per lot (no ongoing testing)	LH054	PFAS QC	Lot, preparation reagents/volumes, date
Cryovials	1 mL methanol	3 per lot (no ongoing testing)	LH054	PFAS QC	Lot, preparation reagents/volumes, date
Autosampler vials	Fill with methanol	3 per lot (no ongoing testing)	LH054	PFAS QC	Lot, preparation reagents/volumes, date
Syringe-driven filters	1 mL methanol	3 per lot (no ongoing testing)	LH054	PFAS QC	Lot, preparation reagents/volumes, date

Methanol	15 mL	2 replicates per lot (no ongoing testing)	LH054	PFAS QC	Lot, preparation reagents/volumes, date
Ammonium Hydroxide	Test as methanolic ammonium hydroxide, 15 mL	2 replicates per lot (no ongoing testing)	LH054	PFAS QC	Lot, preparation reagents/volumes, date

Appendix E. NTN Sample Flow



Appendix F. Sample Notes Codes for Networks

Appendix F1. NTN Sample Notes Codes

NTN Notes and Quality Rating Codes

NTN Sample Condition Codes		
Notes	**Description**	**QR Code[1]**
a	Incomplete laboratory analysis	B
b	Bulk sample (sample exposed the entire time)	C
c	Contaminated sample	C
d	Visible debris in sample	B
e	Extended sampling period (>194 hrs.)	C
f	Field protocol error - Serious problems in field operations that compromise sample integrity; OR - Extended field hold time = Sample receipt > 60 days after OFF date	C

h	Sample handling issue
	- Handling contamination in the field
	- Significant leakage upon receipt in the lab OR
	- Extended field/lab hold times
	  ○ Sample receipt 16-60 days after OFF date
	  ○ Lab analysis date > 30 days from sample receipt
		B

i	Low volume (diluted) sample	B
l	Laboratory error (major handling problems in lab)	C
m	Missing data	B
n	No sample submitted	C
p	Precipitation value unknown (no precipitation data from rain gage or alternate source)	C
q	Minor quality control issue	B
u	Undefined sample (sample exposed for at least 6 hours without precipitation)	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 – Valid data
B – Valid data with minor issues
C – Invalid data

Appendix F2. AMoN Sample Notes Codes

AMoN Notes and Quality Rating Codes

AMoN Sample Condition Codes		
Notes	**Description**	**QR Code[1]**
a	Incomplete laboratory analysis	C
c	Contaminated sample (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	Extended sampling period (>720 hrs.)	C
f	Field protocol error Serious problems in field operations that compromise sample integrity or Extended field hold time = sample receipt > 60 days after OFF date	C
h	Sample handling issue ○ Handling contamination in the field OR ○ Extended sampling/field/lab hold times - Sampling period 360-720 hrs. (15 – 30 days deployed) - Sample receipt 30-60 days after OFF date - Lab analysis date > 30 days from sample receipt	B
l	Laboratory error (major handling problems in lab)	C
m	Missing data	B
n	No sampler deployed	C
q	Minor quality control issue	B
s	Short sampling period (< 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

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

Appendix F3. MDN Sample Notes Codes

MDN Notes and Quality Rating Codes

MDN Sample Condition 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 (> 360 hours/15 days)	C
f	Field protocol error - Serious problems in field operations that compromise sample integrity OR - Extended field hold time = Sample receipt > 60 days after OFF date	C
h	Sample handling issue - Handling contamination in the field - Significant leakage upon receipt in the lab OR - Extended sampling/field/lab hold times o Sampling period 194-360 hrs. o Sample receipt 16-60 days after OFF date o Lab analysis > 60 days from BrCl preservation	B
i	Low volume sample (sample volume < 10ml)	B
l	Laboratory error (major handling problems in lab)	C
m	Missing data	B
n	No sample submitted	C
p	Precipitation value unknown (no precipitation data from rain gage or alternate source)	C
q	Minor quality control issue	B
u	Undefined sample (sample exposed for at least 6 hours without precipitation)	C
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 – Valid data
B – Valid data with minor issues
C – Invalid data

Appendix F4. MLN Sample Notes Codes

MLN Sample Condition Notes Codes		
Notes	**Description**	**QR Code[1]**
f	Field protocol error (serious problems in field operations that compromise sample integrity)	C
i	Low mass sample (sample mass < 10g)	B
l	Laboratory error	C
q	Minor quality control issue	B
[1]Quality Rating (QR) Code Definitions: A – Fully qualified data B – Valid data with minor issues C – Invalid data		

Appendix F5. PFN Analytical Flags

Flag code	Description	Considerations for invalidating**
*QCSL	LCS Accuracy Low	Not invalidating if explainable or justifiable (e.g., surrogate recovery is acceptable or analyst spiking error)
*QCSU	LCS Accuracy High	Not invalidating if explainable or justifiable (e.g., surrogate recovery is acceptable or evapoconcentration of spike suspected)
*SRL	IS Recovery Low	Automatically invalidating
*SRU	IS Recovery High	Not invalidating if explainable (e.g., evapo-concentration of surrogate was observed due to re-injection)
*CCVL	CCV Accuracy Low	Automatically invalidating unless an adjacent positive control suggests that the CCV replicate is anomalous and should be rejected.
*CCVU	CCV Accuracy High	Not invalidating if sample result is below MRL
*B	Compound detected in blank >2x MDL or >1/5 sample concentration	Automatically invalidating, unless the sample result is below detection
*TIR	Transition Ion Ratio Failure	Automatically invalidating
*DUP	Duplicate RPD failure	Not invalidating, but prompts a root cause investigation.
***INV**	**Invalid result**	**This flag will accompany all other flags that contributed to deciding to invalidate the result.**

**Analytical flags are assigned at the analyte level (not the whole sample). Most failures are not automatically invalidating. Failures are discussed during peer review and in meetings with the lab

manager and QA manager, and decisions to invalidate results are made jointly. Considerations made for accepting flagged results are recorded in LIMS.

Appendix G. QC Standards Tables

Appendix G1. NTN and AMoN Control Limits

NADP Combined NTN/AMoN Control Limits						
Version 41		1/9/2026	Round to 3 decimal places per rounding rules below			
ICP	ID	Criteria	Ca	K	Mg	Na
TV (Acceptance Range)	FBFB2101	±MDL	0.000 (-0.008 to 0.008)	0.000 (-0.006 to 0.006)	0.000 (-0.004 to 0.004)	0.000 (-0.008 to 0.008)
	FR50260#	±MDL	0.130 (0.122 to 0.138)	0.022 (0.016 to 0.028)	0.023 (0.019 to 0.027)	0.060 (0.052 to 0.068)
	FLFL2101	80-120%	0.050 (0.040 to 0.060)	0.050 (0.040 to 0.060)	0.050 (0.040 to 0.060)	0.050 (0.040 to 0.060)
	FMFM2101	90-110%	0.500 (0.450 to 0.550)	0.500 (0.450 to 0.550)	0.500 (0.450 to 0.550)	0.500 (0.450 to 0.550)
	FMDL260#	70-130%	0.028 (0.020 to 0.036)	0.010 (0.007 to 0.013)	0.012 (0.008 to 0.016)	0.020 (0.014 to 0.026)
FIA	ID	Criteria	NH_4	OPO_4		
TV (Acceptance Range)	FBFB2101	±MDL	0.000 (-0.014 to 0.014)	0.000 (-0.010 to 0.010)		
	FR50260#	90-110%	0.250 (0.225 to 0.275)	NA		
	FLFL2101	80-120%	0.050 (0.040 to 0.060)	0.030 (0.024 to 0.036)		
	FMFM2101	90-110%	0.600 (0.540 to 0.660)	0.200 (0.180 to 0.220)		
	FMDL260#	70-130%	0.029 (0.020 to 0.038)	0.024 (0.017 to 0.031)		
IC	ID	Criteria	Cl	SO_4	NO_3	
TV (Acceptance Range)	FBFB2101	±MDL	0.000 (-0.020 to 0.020)	0.000 (-0.020 to 0.020)	0.000 (-0.020 to 0.020)	
	FR50260#	90-110%	0.100 (0.090 to 0.110)	0.958 (0.862 to 1.054)	0.898 (0.808 to 0.988)	
	FLFL2301	80-120%	0.050 (0.040 to 0.060)	0.050 (0.040 to 0.060)	0.050 (0.040 to 0.060)	
	FMFM2101	90-110%	0.500 (0.450 to 0.550)	0.500 (0.450 to 0.550)	0.500 (0.450 to 0.550)	
	FMDL260#	70-130%	0.050 (0.035 to 0.065)	0.078 (0.055 to 0.101)	0.031 (0.022 to 0.040)	
AMoN	ID	Criteria	NH_4			
TV (Acceptance Range)	FBFB2101	±MDL	0.000 (-0.014 to 0.014)			
	FR50260#	90-110%	0.250 (0.225 to 0.275)			
	FLFL2101	80-120%	0.050 (0.040 to 0.060)			
	FMAM2101	90-110%	0.750 (0.675 to 0.825)			
	FMDL260#	70-130%	0.029 (0.020 to 0.038)			

QC ID		Description	LDR/Carryover
FBFB2101		Calibration Blank - Type 1 Water.	AMoN LDR= **9** mg/L; No Carryover up to **10** mg/L
FR50260#		Faux Rain Solution - ~50% NTN Concentration.	NTN Lachat PO4 LDR=N/A (2nd order); No Carryover up to **2.829** mg/L (2nd order) NTN Lachat NH4 LDR= **10** mg/L and no carryover up to **10** mg/L (linear)
FLFL2101		Quality control sample at low level - second source.	ICP LDR= Mg=**10** mg/L, K,Ca, Na = **20** mg/L ; No carryover up to **15** mg/L
FMFM2101		Quality control sample at mid level - same source as curve.	IC LDR= **12** mg/L (quadratic), **15** mg/L (linear). No carryover to **12** mg/L (quadratic)
FMAM2101		Quality control sample at mid level - for AMoN (NH_4 only no PO_4) - same source as curve.	Round to 3 decimal places using even/odd rounding rules
FMDL260#		Faux Rain Solution - 2-5 times the expected MDL_N concentration	FMDL Criteria is +/- 30% FCRM is +/- 15% but neither are used for run acceptance

Rounding: Last digit < 5 round down; > 5 round up; IF = 5 use EVEN down/ODD Up rounding i.e. 0.255 = 0.26 and 0.245 = 0.24

Appendix G2. MDN Control Limits

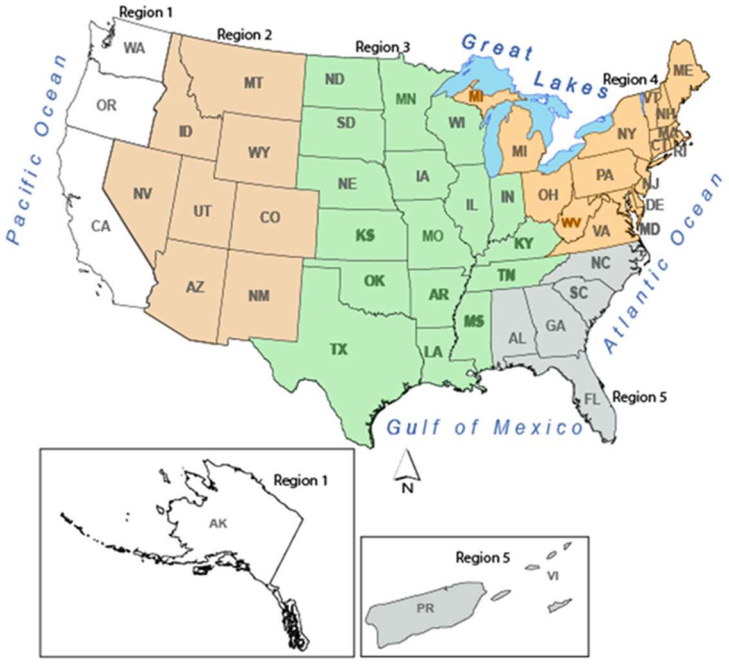
MDN Analytical QC	Revision 6/6/22				
Total Hg Run ID	LIMS ID	True Value (ng/L)	Criterion (% or ng/L) Total Hg	Frequency of Testing	LIMS Criteria CL (1/3 criteria = WL)
Calibration blank (CB)	FCB19001	0.0	Mean < 0.5 ng/L	3 each analytical run	0.5/0.166
Continuing Calibration Blank (CCB)	FCCB1901	0.0	<0.2 ng/L	After calibration; Every 10 samples	0.2/0.0667
Ongoing Precison and Recovery (OPR5)	FOPR1901	5.0	80-120% (must be 90-110% for calibration verification or recalibration required)	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 preparation batch	0.2/0.0667
Digested Quality Control Standard (DQCS - 2nd source)	FQCS1901	8.0	80-120%	1 each preparation batch	1.6/0.533
Matrix Spike/Matrix Spike Duplicate MS/MSD (Compare)	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)	1 each preparation batch	0.1/0.033

Appendix G3. PFN Control Limits

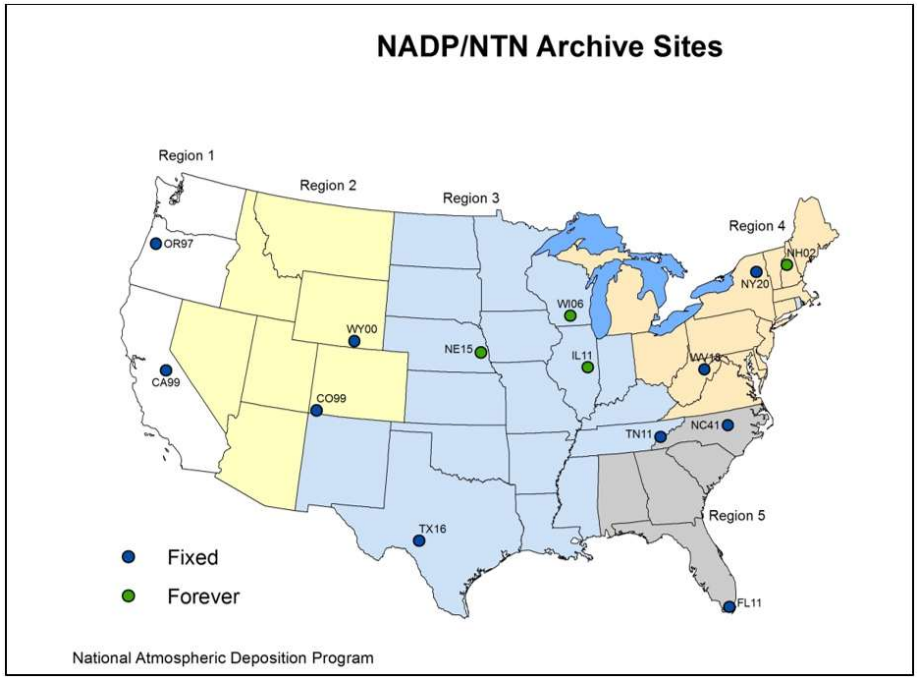
Control Type	LIMS Descriptor	Acceptance Criteria
Method Blank	MB	Any compound that is detected must be < 2x the MDL or <1/5 sample concentration.
Laboratory Control Spike	LCS-1	60-135% of true value
Surrogates	Not applicable	For all extracted samples, including MB and LCS, 25-150%, except for the five neutral compounds (N-MeFOSA, N-EtFOSA, N-MeFOSE, N-EtFOSE, and PFOSA) where surrogate recovery should be 10-150%
Continuing Calibration Verification	CCV	70-130% of true value
Transition Ion Ratio	Not applicable	Transition ion ratio must be 50-150% for analytes above the MDL.
Duplicates	DUP	RPD ≤ 30% for results at or above the 2x MRL. RPD ≤50% for results below 2x MRL.
Continuing Calibration Blank	CCB	<MDL

Appendix H. Archive Maps and Information

Appendix H1. NADP Archive Regions



Appendix H2. "Fixed" and "Forever" Archive Sites



Appendix H3. NADP "Fixed" 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	Yes	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

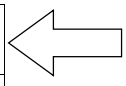
EEMS = Meets siting criteria and is well operated and maintained per EEMS site audits

Appendix H4. 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 H5. NADP Past Archive Policies

NTN Past Archive (Prior to 2019)

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 H6. 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.

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 I. NADP LAB QAP Acronyms

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