## 2020 Quality Assurance Report

January 01 – December 31, 2020

National Atmospheric Deposition Program

**Central Analytical Laboratory** 

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## Central Analytical Laboratory (CAL) Quality Assurance Report (QAR)

January 1 – December 31, 2020

#### 1. Overview

The CAL provides sample processing, chemical analysis, and data validation services for precipitation samples collected by the NADP/National Trends Network (NADP/NTN), and for passive air ammonia samplers for the NADP/Ammonia Monitoring Network (NADP/AMON). The CAL was challenged in 2020 by the unprecedented circumstances brought on by the Covid-19 pandemic. Addressing supply chain issues as well as managing laboratory logistics to help maintain safety within the CAL at the Wisconsin State Laboratory of Hygiene (WSLH) was required to ensure continuity of the networks. All CAL personnel adapted admirably to the changing circumstances and continued to provide the mission critical services required to maintain network operations. Despite the challenging times, the CAL initiated many special projects in 2020, including providing support for per/polyfluoroalkyl substances (PFAS) research at several NTN sites and is developing a secondary sampler that can be attached to NTN buckets for alternate sample collection and analysis (e.g. Total Nitrogen and Phosphorus). The CAL has developed a standard set of laboratory qualifying statements for lab issues that will be incorporated into the NTN QR sample coding (as well as provide additional information to the client). The CAL sample load continues to hold steady for NTN and continues to increase for AMON.

### 2020 CAL Staff

- Systems QA and Special Projects Manager Martin Shafer
- Laboratory Manager Chris Worley
- Sample and Data Processing Manager Amy Mager
- QA Manager Camille Danielson
- Assistant Data Manager Zac Najacht
- Assistant Data Manager Dana Grabowski
- Chemists Katie Blaydes, Jesse Wouters, Nichole Davis (as of 2020), Marie Assem
- Associate Chemists James Sustacheck, Erin Pierce, Chris Lepley (new 2020), Margaret Johnson (new 2020)

## 2. Sample Counts – NTN and AMoN Sample Volume

The total number of network samples received and processed by the CAL is tracked in real-time; however, the percentage of valid samples can only be determined after data are published to the Program Office (PO). Sample numbers listed in **Table 1** include dry and trace samples. A dry sample is from a sampling period without precipitation, and only a field form is submitted to the CAL. In 2020, a trace sample was re-defined as one with less than 4 mL of sample (prior to 2019, a trace sample was defined as <1 mL). All samples equal to or over 4 mL in total volume are classified into the wet sample categories (shown below).

NTN Volume Assessment - Lab Codes (for sample volume):

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

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Valid samples include all samples that received a Quality Rating (QR) of "A" or "B". While a quality rating of "C" is invalid. Very few criteria currently result in invalidation of AMoN samples; therefore, less than 1% were invalidated as can be seen in **Table 2.** Following the tables, **Figure 1** shows active sites, total sample numbers, valid and invalid counts, for the past 5 years for NTN while **Figure 2** depicts these same metrics for the AMoN. The percentage of valid NTN samples has remained consistent at just over 80% for the past 5 years.

| Year | Active<br>Sites | Total<br>Samples | Wet S<br>Number | amples<br>Percent | Trace Samples<br>Number Percent |   | Dry Samples<br>Number Percent |   | Valid Samples<br>Number Percent |    |
|------|-----------------|------------------|-----------------|-------------------|---------------------------------|---|-------------------------------|---|---------------------------------|----|
| 2016 | 272             | 13758            | 11280           | 82                | 411                             | 3 | 2067                          | 2 | 11874                           | 86 |
| 2017 | 274             | 13569            | 10708           | 79                | 487                             | 4 | 2073                          | 2 | 11248                           | 83 |
| 2018 | 262             | 13107            | 9912            | 76                | 413                             | 3 | 1882                          | 1 | 10337                           | 79 |
| 2019 | 256             | 12945            | 10363           | 80                | 142                             | 1 | 1878                          | 1 | 10426                           | 81 |
| 2020 | 257             | 12791            | 9796            | 77                | 231                             | 2 | 2173                          | 2 | 10430                           | 82 |

 Table 1.
 NTN Total Sample Counts 2016-2020

 Table 2.
 AMoN Sample Count 2016-2020

| Voor | ANAON Sitos | # of Sample Sate | Valid Samples |         |  |
|------|-------------|------------------|---------------|---------|--|
| fear | AWON SILES  | # 01 Sample Sets | Number        | Percent |  |
| 2016 | 103         | 2598             | 2580          | 99.3    |  |
| 2017 | 108         | 2529             | 2497          | 98.7    |  |
| 2018 | 103         | 2579             | 2551          | 98.9    |  |
| 2019 | 107         | 2665             | 2643          | 99.2    |  |
| 2020 | 111         | 2760             | 2735          | 99.1    |  |

Note: Sample set is data set for a single site for a single deployment and can include just one single sampler or may include duplicates and/or travel blanks. This table is based on the Sample Set or "N" number.

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Figure 2. Total Valid and Invalid AMoN Samples from January 2016 - December 2020.

### 3. Network Operations

Currently there are two NADP networks that the CAL has responsibility for. The NTN has been in operation for 42 years, while the AMoN has been operating for 13 years. The AIRMON ended operation in September of 2019. **Table 3** shows the total number of samples (including dry and trace) received by the CAL through December 2020 since inception of the networks. **Figure 3** depicts the numbers of active sites per network per calendar year.

| Network | Date Network | Date Network          | Number of Years | Total   |
|---------|--------------|-----------------------|-----------------|---------|
|         | Began        | Ended (if applicable) | in Operation    | Samples |
| NTN     | 7/5/1978     | Continuing            | 42              | 477,498 |
| AMoN    | 10/29/2007   | Continuing            | 13              | 39,919  |
| AIRMoN  | 9/23/1992    | 9/1/2019              | 27              | 7,709   |
| TOTAL   |              |                       |                 | 525,126 |

Table 3. Total Number of Samples in the History of CAL/NADP by Network (All Samples Received < 1/2021)

## 3.1. Active Sites

The number of field sites in each network has varied from year to year. AMoN has seen steady growth while NTN remains relatively constant.



Figure 3. Active Sites per Network per Year.

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## 4. Major Changes

Significant changes that occurred in the CAL during 2020 are recorded in **Table 4**. These are normally changes in protocol or networks of a significant magnitude.

## Table 4. Major CAL Changes 1/1/2020 to 12/31/2020

| NADP Major CAL Related Changes (Rev 9/23/2021) |  |  |                     |  |  |  |  |  |
|--|--|--|---------------------|--|--|--|--|--|
| Date   | Change   | Reason   | Highest<br>Approval |  |  |  |  |  |
| 1/1/2020                                       | WI WD Protocol Changed to Syringe filter   | To treat all samples with filtration and allow enough<br>volume to do all chemical analysis                | Exec                |  |  |  |  |  |
| 1/1/2020                                       | Trace samples changed to < 4 mL, WI 4-13, WD 14-27 and W>27  | To enable us to have sufficient volume for analyses  | Exec                |  |  |  |  |  |
| 1/1/2020                                       | AMoN field QC changed from triplicates to duplicates at 15% of<br>sites  | To improve efficiency while still providing enough field QC  | Exec                |  |  |  |  |  |
| 1/6/2020                                       | Changed holding time for reagents and standards for LACHAT<br>FIA (NH4/ PO4) to 3 weeks  | Testing demonstrated no changes in reagents over 3 weeks   | CAL<br>Management   |  |  |  |  |  |
| 2/4/2020                                       | pH Calibration changed to 4.1 and 6.96 - was set to 7.0 and 4.0 in default calibration since 2018  | Error discovered when troubleshooting bias   | WSLH<br>Management  |  |  |  |  |  |
| 2/25/2020                                      | Started Analysis with extended ammonium calibration curve for<br>FIA AMoN  | Testing demonstrated good results with less need for<br>dilutions  | CAL<br>Management   |  |  |  |  |  |
| 2/26/2020                                      | Moved NTN Filtering to new lab in 135  | Larger space separated from dirty supply cleaning  | WSLH<br>Management  |  |  |  |  |  |
| 3/5/2020                                       | Moved pH and Conductivity analysis to 135  | Larger space separated from dirty supply cleaning  | WSLH<br>Management  |  |  |  |  |  |
| 4/14/2020                                      | <ul> <li>Limit field QC to 4-5 travel blanks per deployment and 0 duplicates.</li> <li>Large batches of samplers will be prepared 3/16/2020 and 3/23/20202 which will cover at least the next four deployments (May26 being the 4th). They will be stored in the freezer until shipped.</li> <li>We will likely continue to store larger than usual batches of samplers that are prepped when possible.</li> </ul> | Precautionary step taken to prevent supply issues due to<br>Covid 19                                       | WSLH<br>Management  |  |  |  |  |  |
| 5/6/2020                                       | AMON new criteria changed for QCs (e.g. FB190001 changed from 0.016 mg/L to 0.013 mg/L)  | Change due to MDL change   | CAL<br>Management   |  |  |  |  |  |
| 5/11/2020                                      | AMON back to normal preparation, starting preparation for 06/09/20 deployment on 05/11/20 and completed on 05/13/20  | Supplies well stocked  | CAL<br>Management   |  |  |  |  |  |
| 8/4/2020                                       | Changed AMoN QC procedures to use Radiello test tubes for all QC samples as well as extracted filter samples.  | Issues with test tubes led to this change  | CAL<br>Management   |  |  |  |  |  |
| 8/21/2020                                      | First day of implementing new expiration dates for only AMON<br>Phenolate reagent. 2 expiration dates: one for AMON (1 week<br>expiration date ) and one for NTN samples ( 3 weeks expiration<br>date)   | Testing verified this change was ok and leads to efficiencies  | CAL<br>Management   |  |  |  |  |  |
| 9/1/2020                                       | Vins NTN sampling bag approved and start using at 06WI -<br>rollout for network in planning phase. WI06 still bucket sampling  | Switching to bags will save resources (even bags since buckets were bagged), staff time and shipping costs | Exec                |  |  |  |  |  |
| 10/20/2020                                     | MN08 first site to begin deployment of Vins bags   | Switching to bags will save resources (even bags since buckets were bagged), staff time and shipping costs | Exec                |  |  |  |  |  |

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### 5. Annual Management Review Summary

All sections of WSHL EHD complete an annual management review to track changes in their section, document audits and issues to address. This is done by the CAL management and approved by the EHD director. An excerpt of this report is shared here.

Dates covered by review: January 1, 2020 to December 31, 2020 Department: NADP (CAL) Person responsible for department's review: Chris Worley and Amy Mager Note: this summary was condensed from original report

#### 5.1. Status of policies/procedures including updates and new procedures that need to be written:

- 5.1.1. Annually, NADP staff are required to sign off that they have reviewed the following WSLH and NADP policy documents: Safety Checklist, Chemical Hygiene Plan, Data Integrity Policy, NADP CAL QA Plan, Emergency Action Plan, HIPAA Refresher, Disability/Accommodation training, Occurrence Reporting Procedure, Occurrence System Management Policy, and Lab wide Accident Reporting (**this all has been completed for 2020**).
- 5.1.2. CAL staff are required to read those SOPs that apply to their routine and backup work duties. Each applicable SOP must be reviewed (and review documented) within a month of taking on a new task/responsibility. These SOPs must be reviewed annually in order to continue with that same responsibility. When a new SOP revision is available, relevant staff must review the latest revision within a month of the new revision date (and document this has been completed).
- 5.1.3. All analytical, sample preparation, NTN and AMoN data review, and sample receiving SOPs have been completed. We are working on the following SOPs: MDLs, Trouble Tickets, NADP LIMs Management, and NADP Data Management/Backup.

#### 5.2. Reports from managerial and supervisory personnel:

#### CAL-Agriculture Drive.

- 5.2.1. **Staffing.** We continue to improve processes and efficiencies. All chemists have rotated to their 3rd analytical platform successfully. Nichole Davis (from CAL-HM) replaced April Grant as one of our Chemists in early 2020.
- 5.2.2. Audits. No external audits were performed during this period. However, Camille Danielson (QA Manager) did perform a broad QA system internal audit of the CAL, HAL and some parts of the PO. See section below for details. The 2019 internal audit was closed out during this period (2020).
- 5.2.3. **New Instrumentation**. An additional Ion Chromatography instrument was purchased for overflow, backup and research applications (installed 10/14/2019). The entire instrument was replaced in 2020 due to noisy baseline issues that could not be resolved. We finally have 3 ICs working well!
- 5.2.4. **Pandemic Impacts.** The AMoN and NTN networks were not significantly impacted by the pandemic. We saw very little in the way of decreased sample loads (approx. 10% max.). NADP staff were provided options of alternate work schedules to minimize in person interactions

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during the pandemic. All NADP CAL functions continued to operate normally. We continue to meet analytical data turnaround goals for AMoN and NTN samples.

- 5.2.5. **Major Network Changes.** EPA continues to hold preliminary discussions on a significant expansion of the AMoN network (100+ additional sites). The CAL moved to a NTN bag collection system beginning in October 2020 to help reduce shipping costs as well as personnel dedicated time for bucket cleaning and preparation.
- 5.2.6. CAL, HAL, PO staff, along with UW-Madison contractors, have been working to modify/improve the NADP website to make it mobile friendly as well as more user friendly. Progress has been made and is currently in the Beta testing phase.
- 5.2.7. The CAL and PO have committed some time/resources to a Total Phosphorus/Total Nitrogen secondary sampler to be used in conjunction with the NTN sampler bucket. Katie Blaydes has been working on an analytical TN/TP method development on our Lachat FIA system. This has the potential to increase capabilities for the CAL. The CAL has also been working on a method to recoat and reuse the AMoN-Radiello sample core to help reduce costs (this is still in the development stage).

CAL-Data Management:

- 5.2.8. **Data Review**. In 2020, the CAL data review group was turning around data to the Program Office within 120-170 days from the month of sample receipt. This was slower than in the previous year due mostly to staff resources redirected to development of the HAL LIMS and improvements to the data reporting process. These demanded time of both data managers, which resulted in a temporary slow-down in data reporting. The COVID 19 pandemic also created staff shortages, which took time away from the Data Processing Manager to devote to helping with data review and reporting. During the last 3-4 months of 2020, turnaround times began trending downward especially for AMON, which reached a 90 day turnaround time in December 2020. The data team and the field operations team began holding combined weekly team meetings which have helped address field issues in a timely manner and help streamline data review.
- 5.2.9. The data team continues to look for avenues to improve data quality; the data review process and how final data results are presented to the customer. A meeting will be held in early 2021 to address implementing an "Initial Review" process where field operations data are reviewed and approved prior to analytical review to further speed up the data review process.

### CAL-Henry Mall (sample receiving and initial chemistry):

5.2.10. **Staffing.** In March 2020 the sample receiving team lost two of its chemists to promotion within the NADP program. Then the pandemic hit and a hiring freeze was put in place. From March through August 2020, the receiving team consisted of just three people (two Associate Chemists and the Sample and Data Processing Manager). A chemist from the WOHL division of the WSLH was temporarily re-assigned to NADP from May through August. In August, two Associate Chemists were hired (Chris Lepley and Margaret Johnson). In November, Colin Kelly began performing supply receiving, washing and shipping duties.

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- 5.2.11. Network Operations. The transition to bag sampling for the NTN network began in October 2020 and by December 2020, approximately 75% of the NTN sites had switched to bag sampling. Sites doing PFAS analysis have continued to use buckets for sampling.
- 5.2.12. **Sample Archive Program**. In early 2021, work will begin to pull the long term archive (fixed and forever) samples out of the archived ICAL samples, and the ICAL long-term archive will be moved from the UW Biotron to Henry Mall. The IL11 archive samples will also be transferred to the CAL in early 2021.

### 5.3. Internal Audits

- 5.3.1. Camille Danielson (QA Manager) conducted a "big picture" look at our QA systems in place for the CAL/HAL/PO.
- 5.3.2. Internal Systems Audit Findings (CAL related):
  - a. Finding 1 Description: NADP NTN and AMoN Data Review SOPs 301 and 302 need to be reviewed and updated. An SOP documenting SOP management needs to be written once Onbase is functional. A table of contents of all NADP spreadsheets needs to be developed.
  - b. Finding 2 Description: Need to develop a customer survey regarding lab/data reporting performance.
  - c. Finding 3 Description: Issues with sample traceability for AMoN and MDN. AMoN and MDN SAMPLE IDs are not provided on the NADP website (nor is AMoN on reports). There are inconsistencies with providing QR C data on the web. AMoN analytical results (mg/L) are provided for ALL samples; NTN data is provided on the web as Valid or Invalid with no actual analytical data given for invalid and MDN is provided on the web in two ways with and without QR C results (with a disclaimer). There is a need for consistency, transparency and more robust qualifying for all the networks.
  - d. Finding 4 description: Lacking SOP on internal audit procedure.
  - e. Finding 5 Description: Need procedures for estimating uncertainty.
  - f. Finding 6 description: Equipment list is not up to date.
  - g. Finding 7 Description: Thermometers are overdue for verification and lacking documented procedures for these tasks.
  - h. Finding 8 Description: NADP Electronic Lab Notebook (ELN) was reviewed as part of this process and some errors in records were found.
  - i. Finding 9 Description: NTN sample results below the MDL have not been correctly reported in italics on preliminary reports.
  - j. Finding description: AMoN samples reported as QR A that should have been QR B N20001438, 20003853 and 20003854, due to duplicate failure.
  - k. Finding 10 Description: MDN and NTN Metadata on the website is outdated and has no document control (i.e. revision date or ID).

| Table 5. | Major corrective and | preventive actions that we | ere implemented dur | ing 2020 in the CAL. |
|----------|----------------------|----------------------------|---------------------|----------------------|
|----------|----------------------|----------------------------|---------------------|----------------------|

| Occurrence<br>Number | Priority | Status   | Subject  | Last Edit<br>Date | Date<br>Submitted | Assignees   |
|----------------------|----------|----------|--|-------------------|-------------------|---|
| <u>3720</u>          | Medium   | Closed   | NADP Unsatisfactory PT for pH                                  | 06/11/2020        | 12/10/2019        | Danielson, Camille G., Worley, Chris  |
| <u>3736</u>          | Medium   | Closed   | NADP permanent change to WI and WD sample processing 1/1/2020  | 03/12/2020        | 01/02/2020        | EHD: Webb, David A. Individual Users:<br>Worley, Chris, Danielson, Camille G. |
| <u>3743</u>          | Medium   | Closed   | NADP Spilled WI sample during<br>processing                    | 03/12/2020        | 01/16/2020        | Danielson, Camille G., Worley, Chris  |
| <u>3790</u>          | Medium   | Closed   | NADP: Blank failure at end of conductivity run, no re-run      | 03/12/2020        | 02/11/2020        | Danielson, Camille G.   |
| <u>3822</u>          | Medium   | Closed   | NADP QA Samples incorrectly stored<br>at room temperature      | 03/12/2020        | 03/05/2020        | Danielson, Camille G., Worley, Chris  |
| <u>3841</u>          | Medium   | Closed   | NADP failed conductivity duplicate                             | 06/11/2020        | 03/25/2020        | Danielson, Camille G., Worley, Chris  |
| <u>3854</u>          | Medium   | Closed   | NADP AMoN Preparation and Field QC<br>Modified due to Covid 19 | 06/11/2020        | 04/02/2020        | Danielson, Camille G., Worley, Chris  |
| <u>3923</u>          | Medium   | Closed   | Biotron freezer went down for NADP archive samples             | 10/01/2020        | 06/23/2020        | Danielson, Camille G., Worley, Chris  |
| <u>3941</u>          | Medium   | Closed   | NADP Failing supply QC for AMoN on<br>FIA 1                    | 09/29/2020        | 07/15/2020        | Danielson, Camille G., Worley, Chris  |
| <u>3972</u>          | Medium   | Closed   | NADP: Missing barcode label used on two separate samples       | 09/30/2020        | 08/18/2020        | Danielson, Camille G.   |
| <u>3973</u>          | Medium   | Closed   | NADP: Sample received with two<br>FORFS logged incorrectly     | 09/30/2020        | 08/18/2020        | Danielson, Camille G.   |
| <u>4059</u>          | Medium   | Assigned | NADP pH duplicate failure becoming<br>systematic issue         | 11/20/2020        | 11/20/2020        | Danielson, Camille G., Worley, Chris  |
| <u>4060</u>          | Medium   | Closed   | NADP FBCD2001 Excessive Failures of<br>blank criteria          | 11/25/2020        | 11/20/2020        | Danielson, Camille G., Worley, Chris  |
| <u>4087</u>          | Medium   | Assigned | NADP NTN samples received excessive<br>bubbles                 | 01/04/2021        | 12/30/2020        | Danielson, Camille G., Worley, Chris  |

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#### 5.4. External Audits

5.4.1. No external audits were performed during 2020.

### 5.5. Changes in the volume and type of work during 2020:

5.5.1. The NADP NTN and AMoN networks experienced an approximate 10% decrease in sample volume during certain periods of the pandemic. However, for the full year, there has not been a significant impact on sample volume during 2020. NTN is holding steady and AMoN has gained several new sites. There has also been ongoing discussions of a significant expansion of the AMoN network through EPA (though this has not occurred yet). We continued to meet holding times and supply shipment responsibilities during the challenging year.

### 5.6. Recommendations for improvement:

One request that we frequently hear, is to expand our NTN analytical menu. We have been working on a TN/TP secondary sampler and analytical method to help address client inquiries.

#### 5.7. List of issues regarding resources, staff training, and other QA-related activities:

The 2020 CAL staffing was adequate to address the needs of our customers at the time. If there is a large increase in AMoN sites (discussed above) or other deviations from our current workload status we will need to re-evaluate circumstances. We continue to strive to improve data quality and data presentation to our customers. The Data Quality Objective Summit is just one of our initiatives in working with our data users to determine their needs.

#### 6. Staff Training

In addition to reviewing applicable SOPs, staff must complete annual reviews of the QAP, policies on data integrity, safety, chemical hygiene, and more. A detailed sign off sheet is completed each year by all staff. Analytical staff also complete an annual analytical demonstration of capability (DOC) for each platform they operate. New staff undergo even more rigorous DOC, initial document review and training protocols. Analysts rotate between different platforms usually on an annual basis. This allows for extensive backup capability as well as fresh perspective/ideas for improving the performance and efficiency of each platform.

#### 7. Instrumentation

**Table 6.** NADP Dedicated Major Analytical Equipment

| Analysis  | Туре                                | Species  | Instrument               |
|---|-------------------------------------|--|--------------------------|
| Inductively Coupled Plasma – Optical Emission<br>Spectrometer (ICP-OES) | Base Cations                        | Na <sup>+</sup> , K <sup>+</sup> , Ca <sup>2+</sup> ,<br>Mg <sup>2+</sup>      | Agilent 5100             |
| Ion Chromatography (IC)   | Acid Anions                         | Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup> | 3 Dionex Integrions      |
| Flow Injection Analysis: Precipitation Samples (FIA- NTN)               | NH <sub>4</sub> and PO <sub>4</sub> | NH <sub>4</sub> <sup>+</sup> and PO <sub>4</sub> <sup>3-</sup>                 | Lachat Quik Chem 8500 S2 |
| Flow Injection Analysis: AMoN Extracts (FIA – AMoN)                     | NH <sub>4</sub>                     | NH4 <sup>+</sup>   | Lachat Quik Chem 8500 S2 |
| pH (pH Meter - Manual Method)   | pН                                  | $H^+$  | Mettler S700 Meter       |
| Specific Conductance – (Conductance Probe – Manual Method)              | Specific<br>Conductance             | Charged Anions<br>& Cations  | Mettler S700 Meter       |

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## 8. QA Documents

The NADP CAL Quality Assurance Plan (QAP) was completed on June 20, 2019 (revision 0) and was revised to incorporate the mercury analytical lab (HAL) in 2020 (Revision 1, June 2020). An Annual Management Review (summarized above), QAR and Internal Systems Audit were also completed in 2020. The CAL/HAL QAP contains detailed QA information on all aspects of the CAL.

## 8.1. Standard Operating Procedures

The CAL has prepared the standard operating procedures (SOPs) outlined in **Table 7** as of the QAR date. SOPs are available upon request. The analytical SOPs are revised as necessary in a time-sensitive manner when method updates are introduced and tracked using version control. Staff that work on a particular task are required to review the SOPs annually for those tests or processes and to affirm completion of their reviews. Analytical SOPs are revised and revised annually and a table is maintained showing status of revisions.

| NADP CA       | L St | andard Ope                | erating Procedures Table of Contents                |                                |             |
|---------------|------|---------------------------|---|--------------------------------|-------------|
| Version Cur   | rent | 8/18/2021                 |   |                                | _           |
| SOP<br>Number | V #  | Current<br>Effective Date | Title   | SOP Original<br>Effective Date | Category    |
| 100           | 2    | 7/6/2020                  | Sample Login and Data Entry                         | 3/20/2019                      | Shipping    |
| 101           | 2    | 8/16/2021                 | Sample Coding                                       | 3/18/2019                      | Shipping    |
| 102           | 1    | 7/7/2020                  | AMoN Supply Shipping                                | 6/18/2019                      | Shipping    |
| 103           | 1    | 7/12/2020                 | NTN Shipping and Receiving of Supplies              | 5/10/2019                      | Shipping    |
|               |      |                           |   |                                |             |
| 200           | 2    | 7/30/2020                 | NTN and MDN Supply QC                               | 10/1/2018                      | QA          |
| 201           | 0    | 12/28/2020                | Analyst Training and Demonstration of Capability    | 12/28/2020                     | QA          |
| 202           | 1    | 12/7/2020                 | Peer Review of Analytical Data                      | 4/3/2019                       | QA          |
|               |      |                           |   |                                |             |
| 300           | 1    | 2/19/2021                 | NTN Data Review                                     | 10/30/2019                     | Data        |
| 301           | 1    | 2/19/2021                 | AMoN Data Review                                    | 11/18/2019                     | Data        |
|               |      |                           |   |                                |             |
| 400           | 1    | 2/2/2021                  | Preparation of Passive Ammonia Diffusive Samplers   | 9/4/2019                       | Preparation |
| 401           | 1    | 9/28/2020                 | AMoN Sampler Extraction                             | 10/17/2019                     | Preparation |
| 402           | 2    | 7/30/2020                 | NTN Sample filtration                               | 3/25/2019                      | Preparation |
| 403           | 1    | 7/30/2020                 | NTN Supply Preparation                              | 5/10/2019                      | Preparation |
| 404           | 0    | 4/3/2020                  | Sample Archive Procedure                            | 4/3/2020                       | Preparation |
| 407           | 0    | 7/24/2020                 | CALNAT Sample Preparation                           | 7/24/2020                      | Preparation |
| 500           | 1    | 7/27/2020                 | ICP - OES   | 1/8/2019                       | Analytical  |
| 501           | 2    | 3/4/2020                  | Ion Chromatography                                  | 2/4/2019                       | Analytical  |
| 502           | 1    | 12/11/2020                | Determination of Ammonium by FIA                    | 4/2/2019                       | Analytical  |
| 503           | 1    | 8/14/2020                 | Determination of Ammonium and Orthophosphate by FIA | 4/23/2019                      | Analytical  |
| 504           | 2    | 8/16/2021                 | Measurement of pH                                   | 3/15/2019                      | Analytical  |
| 505           | 2    | 8/2/2021                  | Measurement of Conductivity                         | 4/3/2019                       | Analytical  |

**Table 7**. NADP CAL Standard Operating Procedures Table of Contents (as of 08/2021)

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## 9. NTN Method Detection Limits (MDL)

## 9.1. NTN Lab Method Detection Limits (MDL<sub>L</sub>) – (Spiked Sample Matrix)

The analytical laboratory method detection limit (MDL<sub>L</sub>) is the minimum measured concentration of a substance that can be reported with 99 percent confidence that the measured concentration is distinguishable from respective method blanks. The Lab MDL is calculated using the 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 MDL). The lab MDLs are provided in **Table 8**.

### 9.2. NTN MDL Blank calculations

A minimum of seven calibration blanks are also assessed to determine a lab  $MDL_L$  based on blank measurements (per 40 CFR 136). The blank  $MDL_L$  is determined using the mean of the blanks + blank standard deviation \* t value at 99% confidence per federal MDL protocols. The  $MDL_L$  based on the blanks should be used as the analytical lab  $MDL_L$  if the result is greater than the spiked lab  $MDL_L$  result

#### 9.3. NTN MDL<sub>L</sub> Usage

Analytical laboratory MDLs are a data quality indicator and are reviewed annually by the CAL and revised by the QA Manager as warranted (i.e. a new instrument or a critical new part is installed on an existing instrument). The analytical laboratory MDL is primarily used to validate instruments and is used as a tool for the QA Manager to assess the Network MDLs validity. It is not used for qualifying NTN data.

### 9.4. NTN Network MDL Process

The network specific MDL (MDL<sub>N</sub>) 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 the potential additional uncertainty introduced due to exposure to sample collection equipment and processing. The difference from the lab MDL solution 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. MDLs are assessed annually and if MDL results are within  $+/- \frac{1}{2}$  MDL of the previous year, the MDL values may remain the same for another year.

### 9.5. Network MDL<sub>N</sub> Usage

The MDL process in 2020 was unusually complicated due to the planned transition to bag-lined buckets, from buckets. It was critical and necessary to determine the Network MDLs using the bag-lined buckets and document acceptable comparability with established (bucket-only) MDL<sub>N</sub>s. The 2019 NTN MDL solution was used to assess potential change in MDL<sub>N</sub>s resulting from the change in NTN sampling from buckets to bag-lined buckets. However, 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. Therefore, blanks were then put through the NTN MDL processes to generate more data. A combination of the blank and the MDL solution data (processed using sampling bags) was then used to assess the network MDLs and verify that the MDLs established in 2019 could be used for 2020. The bag analyte loss issue was still being

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investigated at the end of 2020, and the network was continuing to use buckets for the majority of the sites. Therefore, MDLs based on buckets for 2019 were applied to 2020 data.

The MDL<sub>N</sub> is used at the bench to provide reference for routine QC samples. It is also used to censor NTN data published by the PO for samples received in the calendar year. The calendar year is a bit hard to decipher as it depends on the date that the CAL receives the sample. Therefore, the sample IDs for that calendar year are also documented in the Historical MDL table so that it is clear which samples fall into a particular year. The NTN sample results that are less than the MDL<sub>N</sub> for that calendar year are published on the NADP website with the MDL<sub>N</sub> value in place of the measured value and a less than (<) symbol in the column adjacent to the result. For NTN, the **data reported to the sites** in their monthly reports includes the less than MDL<sub>N</sub> values (such data are italicized if less than the NTN MDL<sub>N</sub> for that calendar year).

The most recent NTN network MDLs are provided in **Table 8**, and **Table 9** provides the Network MDLs for NTN from 1987-2020. It should be noted that the 2018 MDLs were established per the readiness verification plan and were unrealistically low.

| Analyte         | 2018    | 2019  | 2020    | 2018    | 2019    | 2020    |
|-----------------|---------|-------|---------|---------|---------|---------|
|                 | Lab     | Lab   | Lab     | Network | Network | Network |
|                 | $MDL_L$ | MDLL  | $MDL_L$ | $MDL_N$ | $MDL_N$ | $MDL_N$ |
| Ca              | 0.004   | 0.001 | 0.008   | 0.011   | 0.023   | 0.023   |
| Mg              | 0.002   | 0.001 | 0.001   | 0.003   | 0.006   | 0.006   |
| Na              | 0.003   | 0.002 | 0.001   | 0.004   | 0.010   | 0.010   |
| К               | 0.002   | 0.003 | 0.002   | 0.005   | 0.005   | 0.005   |
| Cl              | 0.006   | 0.004 | 0.003   | 0.006   | 0.018   | 0.018   |
| SO <sub>4</sub> | 0.008   | 0.007 | 0.005   | 0.007   | 0.018   | 0.018   |
| NO <sub>3</sub> | 0.003   | 0.003 | 0.006   | 0.008   | 0.018   | 0.018   |
| Br              | 0.003   | 0.002 | NA      | 0.006   | 0.006   | NA      |
| NH <sub>4</sub> | 0.004   | 0.002 | 0.007   | 0.008   | 0.017   | 0.017   |
| PO <sub>4</sub> | 0.003   | 0.003 | 0.004   | 0.008   | 0.010   | 0.010   |
| pН              | 0.01    | 0.01  | 0.01    | 0.01    | 0.01    | 0.01    |
| Conductivity    | 0.9     | 0.9   | 0.9     | 0.9     | 0.9     | 0.9     |

### Table 8. NTN MDLs

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| NTN Historical Network Method Detection Limits (mg/L) Revision 8/2021 |               |                        |       |       |       |       |       |       |       |       |       |       |
|---|---------------|------------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Sample Start ID   | Sample End ID | Aproximate<br>Year RCV | Ca    | Mg    | Na    | к     | NO3   | SO4   | Cl    | Br    | NH4   | PO4   |
| NF4631  | NH6700        | 1987-1989              | 0.009 | 0.003 | 0.003 | 0.003 | 0.030 | 0.030 | 0.030 | NA    | 0.020 | 0.020 |
| NH6701  | NM6824        | 1989-1993              | 0.009 | 0.003 | 0.003 | 0.003 | 0.030 | 0.030 | 0.030 | NA    | 0.020 | 0.020 |
| NM6825  | NS3700        | 1993-1998              | 0.009 | 0.003 | 0.003 | 0.003 | 0.030 | 0.030 | 0.030 | NA    | 0.020 | 0.003 |
| NS3701  | NU7200        | 1998-2000              | 0.009 | 0.003 | 0.003 | 0.003 | 0.010 | 0.010 | 0.005 | NA    | 0.020 | 0.003 |
| NU7201  | NW0218        | 2000-2001              | 0.009 | 0.003 | 0.003 | 0.003 | 0.010 | 0.010 | 0.005 | NA    | 0.020 | 0.009 |
| NW0219  | NZ9957        | 2001-2004              | 0.009 | 0.003 | 0.003 | 0.003 | 0.010 | 0.010 | 0.005 | NA    | 0.020 | 0.006 |
| NZ9958  | TA0214        | 2004                   | 0.009 | 0.003 | 0.003 | 0.003 | 0.009 | 0.013 | 0.008 | NA    | 0.020 | 0.006 |
| TA0215  | TA0334        | 2004                   | 0.002 | 0.001 | 0.003 | 0.001 | 0.009 | 0.013 | 0.008 | NA    | 0.020 | 0.006 |
| TA0335  | TB4169        | 2005                   | 0.002 | 0.001 | 0.003 | 0.001 | 0.009 | 0.013 | 0.008 | NA    | 0.005 | 0.006 |
| TB4170  | TE3724        | 2006-2007              | 0.002 | 0.001 | 0.001 | 0.001 | 0.017 | 0.010 | 0.003 | NA    | 0.004 | 0.004 |
| TE3725  | TG9571        | 2007-2009              | 0.006 | 0.001 | 0.001 | 0.001 | 0.009 | 0.010 | 0.004 | NA    | 0.006 | 0.004 |
| TG9572  | TI2460        | 2009-2010              | 0.004 | 0.001 | 0.003 | 0.001 | 0.005 | 0.004 | 0.003 | NA    | 0.010 | 0.008 |
| TJ5599  | TM2704        | 2011-2013              | 0.005 | 0.002 | 0.002 | 0.003 | 0.010 | 0.010 | 0.009 | 0.005 | 0.009 | 0.005 |
| TM2705  | TN2615        | 2014                   | 0.019 | 0.005 | 0.005 | 0.001 | 0.007 | 0.005 | 0.008 | 0.005 | 0.017 | 0.009 |
| TN2616  | TP0369        | 2015                   | 0.009 | 0.002 | 0.006 | 0.002 | 0.005 | 0.005 | 0.005 | 0.005 | 0.016 | 0.005 |
| TP0370  | TQ4360        | 2016                   | 0.009 | 0.002 | 0.003 | 0.004 | 0.005 | 0.004 | 0.005 | 0.004 | 0.019 | 0.005 |
| TQ4361  | TS9999        | 2017                   | 0.006 | 0.002 | 0.002 | 0.002 | 0.005 | 0.005 | 0.003 | 0.004 | 0.018 | 0.006 |
| TT0001  | TT7317        | 2018                   | 0.011 | 0.003 | 0.004 | 0.005 | 0.008 | 0.007 | 0.006 | 0.006 | 0.008 | 0.008 |
| TT7318  | TV0257        | 2019                   | 0.023 | 0.006 | 0.010 | 0.005 | 0.018 | 0.018 | 0.018 | 0.006 | 0.017 | 0.010 |
| TV0258  | TW3112        | 2020                   | 0.023 | 0.006 | 0.010 | 0.005 | 0.018 | 0.018 | 0.018 | 0.006 | 0.017 | 0.010 |

### Table 9. NTN Historical Network MDLs 1987-2020

## **10. AMoN Detection Limits**

### 10.1. AMoN Lab MDL (MDLL)

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

In 2020, the AMoN Lab MDL was calculated as the mean core blank for all available core blanks with results greater than zero. There were 103 valid core blank values from June 2018 – December 2019 and these were used to determine a mean of 0.013 mg/L NH<sub>4</sub> to be used as the MDL<sub>L</sub>. See **Table 10** for other recent AMoN Lab MDLs.

#### 10.2. AMoN Network MDLs 10.2.1. AMoN MDL<sub>N</sub> Calculations

The network specific AMoN method detection limit (AMoN MDL<sub>N</sub>) is calculated annually from valid travel blanks.

The 2020 AMoN MDL<sub>N</sub> was calculated using all valid travel blanks from an approximate 12-month period of the most recent samples for which final data was available. 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. The AMoN MDL<sub>N</sub> = mean valid travel blanks + (s \* t99).

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See Table 10 for AMoN Network MDLs. See Table 11 for a summary of the historical AMoN MDLs.

#### 10.3. Use of AMoN $MDL_N$ for data assessment

The AMoN Network MDL is used to flag data that is below the  $MDL_N$  with a "d" which automatically changes the sample QR code from "A" to "B". Other factors could further reduce the QR to a "C". AMoN data is reported with a QR code and is not "censored" at the  $MDL_N$ .

#### Table 10. AMoN MDLs 2018-2020

| AMoN                 | 2018    | 2019    | 2020    | 2018        | 2019        | 2020        |
|----------------------|---------|---------|---------|-------------|-------------|-------------|
|                      | Lab MDL | Lab MDL | Lab MDL | Network MDL | Network MDL | Network MDL |
| mg/L NH <sub>4</sub> | 0.008   | 0.016   | 0.013   | 0.119       | 0.104       | 0.083       |

Note: The 2018 Lab MDL was based on NTN Lab MDL due to lack of data.

#### Table 11. AMoN Historical MDLs

|              |         | AMoN Histo                   | rical Method Deteo                       | ction Limits                   |                           |
|--------------|---------|------------------------------|--|--------------------------------|---------------------------|
| Sample ID    | Year of | AMoN Network MDL             | AMoN Lab MDL                             | Network MDL Basis              | Lab MDL Basis             |
| Range        | Sample  | (MDL <sub>N</sub> ) mg/L NH₄ | (MDL <sub>I</sub> ) mg/L NH <sub>4</sub> |                                |                           |
|              | Receipt |                              |  |                                |                           |
| All Prior to |         |                              |  |                                |                           |
| N18005002    | <2018   | 0.0469                       | 0.0469                                   | Established by ICAL            | Established by ICAL       |
| N18005002 -  |         |                              |  | ISWS 2017 valid travel blank   | NTN Lab MDL due to lack   |
| N18006407    | 2018    | 0.119                        | 0.008                                    | data                           | of core data              |
|              |         |                              |  |                                | mean core blank value     |
| N19000001 -  |         |                              |  |                                | from June – December      |
| N19002669    | 2019    | 0.104                        | 0.016                                    | All valid 2018 travel blanks   | 2018                      |
|              |         |                              |  |                                | mean core blank value for |
|              |         |                              |  | All valid TB for ~ 12 months   | all available core blanks |
|              |         |                              |  | most recent from 741 valid     | with results greater than |
|              |         |                              |  | travel blanks with "end dates" | zero. N =103 core blank   |
| N2000001 -   |         |                              |  | (end of deployment period)     | values from June 2018 -   |
| N20002856    | 2020    | 0.083                        | 0.013                                    | from June 2018 to June 2019    | December 2019             |

It should be noted that the prior laboratory set the MDLs to 0.0469 mg/L in some unknown manner prior to 2018.

#### **11. External Field QA Programs**

Information for Section 11 is extracted from the USGS External Quality Assurance Project Report for the National Atmospheric Deposition Program's National Trends Network and Mercury Deposition Network.

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## 11.1. The U.S. Geological Survey (USGS) Programs

The USGS used two programs to provide external quality assurance monitoring for the National Atmospheric Deposition Program's (NADP) NTN in 2020. The field audit program assessed the effects of onsite exposure, sample handling, and shipping on the chemistry of NTN samples. The interlaboratory comparison program assessed the bias and variability of the chemical data from the CAL and other participating laboratories that analyze precipitation samples for major ions, and nutrients. See Section 13.

### 11.2. Field Audit Samples

The USGS PCQA program uses equipment-rinse samples (bag and sample train) paired with corresponding deionized water or known concentration solutions to identify changes in chemical contamination levels in the networks. Sites process these samples on dry weeks and send them to the CAL or the HAL. These results are published in an official publication every two years. The 2020 data have not been published but the preliminary results are given below.

### 11.3. 2020 Field Audit Sample Preliminary Conclusions for NTN (per Greg Wetherbee)

- Field Audit samples indicate substantial increases in Network Maximum Contamination Levels compared to previous field audits, especially for Ca, K, Cl, NO<sub>3</sub>, and SO<sub>4</sub>.
- Field Audit samples also indicate increase in H-ion loss, but this might be due to past pH bias at CAL that was corrected.

### 12. Internal Field QA Programs

### **AMoN Travel Blanks and Field Duplicates**

In 2020, ~25% of sites received travel blanks each deployment and sites all received travel blanks several times per year. For deployments in 2020, the CAL switched from triplicate to duplicate samplers to assess precision (after approval from QAAG/Exec). Duplicate samplers were sent to approximately 15% of the sites each deployment, also in a rotating fashion beginning in January of 2020.

### 12.1. Travel Blanks

Over 1000 travel blanks were sent to sites and analyzed between June of 2018 and November of 2019. Travel blanks >0.2 mg/L NH<sub>4</sub> (~0.4  $\mu$ g/m<sup>3</sup> NH<sub>3</sub>) exceed the established maximum blank criterion and must be flagged. There were no valid travel blanks above 0.2 mg/L NH<sub>4</sub> during the reporting period. The mean/median travel blanks have remained very consistent and low (< 1/5<sup>th</sup> criterion). Refer to **Table 12** for the mean, median and maximum travel blank concentrations since the WSLH began operating the AMoN network. Refer to **Figure 4** for the 2020 AMoN travel blanks and **Figure 5** for the AMoN travel blanks since the beginning of the network. Wisconsin State Laboratory of Hygiene NADP CAL 2020 Quality Assurance Report Final Version: 10/27/2021 Page: 19 of 47

#### Table 12. AMoN Travel Blank Results 2018-2020

|  | June 2018- Nov 2019 | 2020     | 2020      |
|--|---------------------|----------|-----------|
|  | mg/L NH₄            | mg/L NH₄ | µg/m³ NH₃ |
| Mean   | 0.036               | 0.037    | 0.069     |
| Median   | 0.033               | 0.033    | 0.060     |
| Мах  | 0.184               | 0.154    | 0.310     |
| Number of Valid Travel Blanks                    | 1029                | 540      | 540       |
| Number of Invalid (QR=C)Travel Blanks (not used) | 8                   | 0        | 0         |



Figure 4. AMoN Travel Blank Ammonia Levels 2020



Figure 5. AMoN Travel Blank Historical Ammonia Levels 2007 - 2020

## **AMoN Field Duplicates**

From August 2018 (triplicates were not started immediately in June of 2018 when the WSLH took over the network operation) through December 2019 there were over 500 sets of valid (not excluded due to major lab or field error) triplicates deployed and assessed. Triplicates (2018 & 2019)/Duplicates (2020) that exceed 15% RSD were retested to ensure it is not an analytical issue and noted in the qualifiers spreadsheet. The results are confirmed every time so we have discontinued this practice. In 2020, the CAL stopped sending triplicates and instead deployed and analyzed 361 duplicate sets.

In 2020, 90% of the replicate sets (across all ambient concentrations) had less than 18% RPD. All duplicate data sets were included in the average and median calculations. However, for assessing RPD it is apparent that the inclusion of low concentration and low absolute difference sets skews the data. This is conveyed in **Table 13-14**, **Figures 6**, and **7**. It is more appropriate to assess the absolute differences (AD) in the concentration, and when you do so, the 95<sup>th</sup> percentile of the set AD was at absolute difference of 0.25  $\mu$ g/m<sup>3</sup> NH<sub>3</sub> and 80<sup>th</sup> percentile was at 0.07  $\mu$ g/m<sup>3</sup> NH<sub>3</sub>. This means that 95% of the sample and duplicate ammonia results were within 0.25  $\mu$ g/m<sup>3</sup> NH<sub>3</sub> of each other.

As can be seen in **Figure 6** and **7**, AMoN duplicate differences are generally very small. The highest absolute differences are most often seen at the higher concentrations while the highest RPD is seen at very low concentrations as one might expect. Field duplicates that are extreme outliers are generally due to field error and have very high RPDs. Often the deviation is due to field or shipping issues (not analytical) as any results above 15% RPD are reanalyzed and confirmed by the CAL.

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Table 13. AMoN Relative Percent Difference (RPD) and Absolute Difference (AD) percentiles

|                 | 2020%           | RPD % | AD µg/m³ NH₃ |  |
|-----------------|-----------------|-------|--------------|--|
| AMoN Duplicate  | 80th Percentile | 9.5   | 0.07         |  |
| Sets 2020 - 361 | 85th Percentile | 11.8  | 0.10         |  |
| Sets            | 90th Percentile | 18.2  | 0.15         |  |
|                 | 95th Percentile | 43.9  | 0.25         |  |

**Table 14.** AMON Average and Median Relative Percent Difference (RPD) and Absolute Difference (AD) of Field Duplicates.

| 2020 Duplicates | RPD % | AD μg/m <sup>3</sup><br>NH <sub>3</sub> |
|-----------------|-------|---|
| Average         | 10.9  | 0.11                                    |
| Median          | 3.7   | 0.02                                    |



Figure 6. Relative percent difference of AMoN Field Duplicate Ammonia Results (n=361 sets)

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Figure 7. Absolute difference of 2020 AMoN Field Duplicates versus Ammonia Concentration (361 sets)

#### **13. Proficiency Test results**

Due to the Covid 19 Pandemic, most formal PT programs were put on hold. The CAL did complete one PT study through the World Meteorological Organization (WMO) in October 2020. The CAL also completed the USGS Interlab Comparison samples. Results provided below.

| PT Provider                             | CAL ID # | PT Studies<br>Completed | Results outside of Control Limits  | Website Results   |
|---|----------|-------------------------|--|---|
| ECCC                                    | F303     | None                    | NA   | Not on website - Available upon<br>Request  |
| WMO Global<br>Atmosphere<br>Watch (GAW) | 700175   | WMO 62                  | 1-pH above control limits  | http://www.qasac-<br>americas.org/study-results   |
| USGS                                    | NA       | 2020                    | Positive, statistically significant analytical bias<br>indicated for cations, ammonium, and H-ion for CAL<br>– but not of practical significance. Negative,<br>statistically significant analytical bias indicated for CI<br>and SO4 for CAL, but not of practical significance. | https://bqs.usgs.gov/PCQA/Interla<br>boratory Comparison/graphOutpu<br>t.php?page=start |

Table 15. 2020 Proficiency Test Results Summary

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USGS Intercomparison preliminary results (Per G. Wetherbee):

• Positive, statistically significant analytical bias indicated for cations, ammonium, and H-ion for CAL – but not of practical significance.

• Negative, statistically significant analytical bias indicated for Cl and SO4 for CAL, but not of practical significance.

• CAL variability is lower than average among all participating labs, and RSD < 5% for all analytes indicates good precision.

WMO PTs There was one exceedance of WMO acceptance criteria for pH sample 1 as seen in purple on the ring diagram in **Figure 8**. In assessing the results, potassium showed a slight low bias, ammonium a very slight high bias and no other analytes demonstrated consistent bias (per WMO no bias was significant). The one orange % recovery from the 2<sup>nd</sup> PT sample for K was deemed ok because the result is within plus or minus the MDL even low recovery is low.



#### Figure 8. WMO PT Results Diagrams and Keys



#### WMO Keys to the Assessment:

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**Good - green hexagon -** A good measurement is within the interquartile range (IQR), defined as the 25th to 75th percentile or middle half of the measurements. For a measurement within the IQR that fails to meet the DQO, the green hexagon has a gray fill (see potassium).

**Satisfactory - green trapezoid -** A satisfactory measurement is outside of the IQR but within the range defined by the median ±(IQR/1.349). The ratio, IQR/1.349, is the non-parametric estimate of the standard deviation, sometimes called the pseudo-standard deviation. A measurement that is outside of the median ±1 standard deviation but meets the DQO is an exception to this definition. It is set automatically to satisfactory. Nitrate and chloride are satisfactory measurements that meet the DQOs. When a satisfactory measurement fails to meet the DQO, the green trapezoid has a gray fill (see magnesium).

**Marginal - purple trapezoid -** A marginal or marginally acceptable measurement is outside the range of satisfactory measurements but inside the range defined by the median ±2(IQR/1.349). Marginal measurements fail to meet the DQOs. Examples are sodium and calcium.

**Biased - red triangle -** A biased measurement is outside the range of marginal measurements ( >2 standard deviations from the median). Biased measurements fail to meet the DQOs. Examples are pH and conductivity.

**Detection Limit - open circle -** Measurement is below the detection limit of the laboratory's analytical method. Fluoride is an example.

No Measurement - circle with slash - Measurement was not reported. Acidity is an example.

Table 16. WMO PT Results CAL Assessment (TV "true value" study mean from the WMO Study)

| PT samples \       | WMO 62 WSL |       |       |        |        |                    |       |        |        |        |       |
|--------------------|------------|-------|-------|--------|--------|--------------------|-------|--------|--------|--------|-------|
| Date               |            |       |       |        |        |                    |       |        |        |        |       |
| Received           | Sample ID  | рН    | Cond  | Ca     | Na     | К                  | Mg    | Cl     | SO4    | NO3    | NH4   |
| 10/6/2020          | WMO62 -1   | 5.36  | 11.1  | 0.384  | 0.213  | 0.060              | 0.073 | 0.353  | 1.340  | 1.496  | 0.493 |
| TV - Final<br>Mean |            | 5.23  | 11.2  | 0.380  | 0.214  | 0.061              | 0.072 | 0.349  | 1.320  | 1.440  | 0.485 |
| % of TV            |            | 102   | 99    | 101    | 100    | 98                 | 101   | 101    | 101    | 104    | 102   |
|                    |            | 0.13  | -0.10 | 0.004  | -0.001 | -0.001             | 0.001 | 0.004  | 0.020  | 0.056  | 0.008 |
| 10/6/2020          | WMO62-2    | 5.15  | 4.5   | 0.043  | 0.016  | 0.008              | 0.009 | 0.037  | 0.266  | 0.326  | 0.078 |
| TV - Final<br>Mean |            | 5.15  | 4.4   | 0.045  | 0.016  | 0.011              | 0.009 | 0.039  | 0.270  | 0.330  | 0.077 |
| % of TV            |            | 100   | 102   | 94     | 101    | 71 - OK +/-<br>MDL | 101   | 96     | 98     | 99     | 102   |
|                    |            | 0.00  | 0.10  | -0.003 | 0.000  | -0.003             | 0.000 | -0.002 | -0.004 | -0.004 | 0.001 |
| 10/6/2020          | WMO62-3    | 4.74  | 11.5  | 0.110  | 0.080  | 0.030              | 0.043 | 0.114  | 1.039  | 1.075  | 0.210 |
| TV - Final         |            | 4 76  | 11 /  | 0 109  | 0.080  | 0.030              | 0.0/3 | 0 118  | 1 020  | 1.060  | 0.205 |
| Mean               |            | 4.70  | 11.4  | 0.105  | 0.080  | 0.050              | 0.045 | 0.118  | 1.020  | 1.000  | 0.205 |
| % of TV            |            | 100   | 101   | 100    | 100    | 99                 | 100   | 96     | 102    | 101    | 102   |
|                    |            | -0.02 | 0.10  | 0.001  | 0.000  | 0.000              | 0.000 | -0.004 | 0.019  | 0.015  | 0.005 |

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#### 14. Analytical Quality Assurance

### 14.1. Analytical Sample Duplicates

Duplicate sample analysis is performed to assess laboratory precision. A second aliquot of a sample is analyzed in the same batch of 10 samples. The precision between the two results is evaluated. Duplicates are chosen at random and must be performed at a frequency of 10%. Refer to **Table 17** for the duplicate acceptance criteria for the ICP, IC and FIA platforms. Criteria for pH and conductivity duplicates is within 0.2 pH units and 1  $\mu$ S/cm, respectively. Exceedance metrics for 2020 are in **Table 18** and show remarkably good precision for a large number of duplicates. Note – the exceedances listed below are failures based on the criteria in **Table 17**. All duplicates that fail to meet Table 17 criteria are rerun if possible. The graphs display what appears to be more duplicate failures because they are only based on RPD. They are not adjusted for samples at or below 10xMDL where AD is more realistic to use for QC assessment (as seen in Tables 17/18).

| Sample Result  | Duplicate Result   | Calculation                                 | Criteria                |
|--|--|---|-------------------------|
|  |  | Alexandre D'fference (AD)                   |                         |
| MDL to TUX MDL   | MDL to TUX MDL   | Absolute Difference (AD)                    | AD must be ±MDL         |
| <mdl< td=""><td>&gt;MDL</td><td>Absolute Difference (AD)</td><td>AD must be ±MDL</td></mdl<>                       | >MDL   | Absolute Difference (AD)                    | AD must be ±MDL         |
|  |  |   |                         |
| <mdl< td=""><td><mdl< td=""><td>AD=ND (Absolute Difference = No Difference)</td><td>Passes</td></mdl<></td></mdl<> | <mdl< td=""><td>AD=ND (Absolute Difference = No Difference)</td><td>Passes</td></mdl<> | AD=ND (Absolute Difference = No Difference) | Passes                  |
| <10x MDL   | >10x MDL   | Relative Percent Difference (RPD)           | RPD must be $\leq 10\%$ |
| >10x MDL   | >10x MDL   | RPD   | RPD must be $\leq 10\%$ |

Table 18. Analytical Duplicates and Percent Exceedances in 2020

| Platform        | # Replicates<br>in 2020 | # Failures<br>in 2020 | % Exceedance<br>(prior to reanalysis) | # Reanalyzed<br>successfully |
|-----------------|-------------------------|-----------------------|---------------------------------------|------------------------------|
| FIA AMoN        | 228                     | 13                    | 5.7%                                  | 13                           |
| FIA NTN         | 1056                    | 4                     | 0.3%                                  | 4                            |
| ICP-OES         | 1335                    | 5                     | 0.3%                                  | 5                            |
| IC              | 1416                    | 2                     | 0.1%                                  | 0                            |
| pH/Conductivity | 1058                    | 71*                   | 6.7 %                                 | 70                           |

\*These are primarily pH failures that were determined to be mostly caused by carryover of the FLPH standard that was routinely analyzed immediately before the first sample in the duplicate and this issue was corrected in 2021 and is dramatically improved.

Note: Some platforms have more Duplicates in a year due to more frequent re-runs of samples, which requires additional duplicates to be analyzed.

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# Figure 9. Sulfate (IC) Sample and Analytical Duplicate relative percent difference of sets at or above the network detection limit.

NOTE –The duplicate graphs here and below show duplicates above 10% RPD which are not technically QC failures if the sample concentration is at or below 10X MDL. In the lab, those are assessed as pass/fail based on the absolute difference being within the MDL per **Table 17**.

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Figure 10. Nitrate (IC) Sample and Analytical Duplicate relative percent difference of sets at or above the network detection limit.



Figure 11. Chloride (IC) Sample and Analytical Duplicate relative percent difference of sets at or above the network detection limit.

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Figure 12. Orthophosphate (FIA) Sample and Analytical Duplicate relative percent difference of sets at or above the network detection limit. Note very few duplicates are displayed here because although over 1000 sets were analyzed only 189 were at or above the MDL.



Figure 13. Ammonium (FIA) Sample and Analytical Duplicate relative percent difference of sets at or above the MDL.

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Figure 14. Calcium (ICP) Sample and Analytical Duplicate relative percent difference of sets at or above the network detection limit.



Figure 15. Sodium (ICP) Sample and Analytical Duplicate relative percent difference of sets at or above the NTN MDL.

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Figure 16. Magnesium (ICP) Sample and Analytical Duplicate relative percent difference of sets at or above the network detection limit.



Figure 17. Potassium (ICP) Sample and Analytical Duplicate relative percent difference of sets at or above the network detection limit.

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Figure 18. Absolute differences between minimum and maximum pH values from duplicate analyses for a particular sample.



Figure 19. Absolute differences between minimum and maximum conductivity duplicate values for a particular sample.

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#### 14.2. Analytical QA and Acceptance Criteria

Each QC solution has a set target value and acceptable range of values based on the applicable criteria (some are +/-10%, MDL etc.). [criteria are further detailed in the CAL/HAL QAPP].

Table 19. Analytical Limits for Internal QC Solutions.

| NADP Combine      | ed NTN/A      | MoN Control Limits ~            | Target Values (Accept                             | able Range)   |                                       |  |
|-------------------|---------------|---------------------------------|---|---|---------------------------------------|--|
| Version 29        | 9/29/2021     | Round                           | to 3 decimal places per rounding rules            | below   |                                       |  |
| ID                | Criteria      | Ca                              | Na  | К   | Mg                                    |  |
| FBFB2101          | ±MDL          | 0.000 (-0.010 to 0.010)         | 0.000 (-0.008 to 0.008)                           | 0.000 (-0.006 to 0.006)   | 0.000 (-0.006 to 0.006)               |  |
| FR50210#          | ±MDL          | 0.130 (0.120 to 0.140)          | 0.060 (0.049 to 0.065)                            | 0.022 (0.016 to 0.028)  | 0.023 (0.017 to 0.029)                |  |
| 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)                |  |
| ID                | Criteria      | NH₄ (NTN ONLY)                  | OPO4  |   |                                       |  |
| FBFB2101          | ±MDL          | 0.000 (-0.014 to 0.014)         | 0.000 (-0.010 to 0.010)                           |   |                                       |  |
| FR50210#          | 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)                            |   |                                       |  |
| ID                | Criteria      | Cl                              | SO₄   | NO3   |                                       |  |
| FBFB2101          | ±MDL          | 0.000 (-0.020 to 0.020)         | 0.000 (-0.020 to 0.020)                           | 0.000 (-0.020 to 0.020)   |                                       |  |
| FR50210#          | 90-110%       | 0.100 (0.090 to 0.110)          | 0.960 (0.864 to 1.056)                            | 0.900 (0.810 to 0.990)  |                                       |  |
| FLFL2101          | 80-120%       | 0.025 (0.020 to 0.030)          | 0.025 (0.020 to 0.030)                            | 0.025 (0.020 to 0.030)  |                                       |  |
| FMFM2101          | 90-110%       | 0.500 (0.450 to 0.550)          | 0.500 (0.450 to 0.550)                            | 0.500 (0.450 to 0.550)  |                                       |  |
| ID                | Criteria      | NH <sub>4</sub> (AMoN ONLY)     |   |   |                                       |  |
| FBFB2101          | ±MDL          | 0.000 (-0.010 to 0.010)         |   |   |                                       |  |
| FR50210#          | 90-110%       | 0.250 (0.225 to 0.275)          |   |   |                                       |  |
| FLFL2101 (low FL) | 80-120%       | 0.050 (0.040 to 0.060)          |   |   |                                       |  |
| FMAM2101          | 90-110%       | 0.750 (0.675 to 0.825)          |   |   |                                       |  |
| QC ID             | Description   |                                 |   | LDR/Carryover   |                                       |  |
| FBFB2101          | Calibration I | Blank - Type 1 Water.           |   | AMoN LDR= 10 mg/L; No Carryover   | up to <b>10</b> mg/L                  |  |
| FR50210#          | Faux Rain So  | olution - ~50% NTN Concentr     | ation.  | NTN Lachat PO4 LDR=N/A (2nd order); No Carryover up to <b>2.829</b> mg/L (2nd order)<br>NTN Lachat NH4 LDR= <b>10</b> mg/L and no carryover up to <b>10</b> mg/L (linear curve) |                                       |  |
| FLFL2101          | Quality cont  | rol sample at low level - seco  | ond source.                                       | ICP LDR= Mg=10 mg/L, K,Ca, Na = 20 mg/L ; No carryover up to 15 mg/L  |                                       |  |
| FMFM2101          | Quality cont  | rol sample at mid level - sam   | ne source as curve.                               | IC LDR= 12 mg/L (quadratic), 15 mg/L (Linear). No carryover to 12 mg/L (quadratic)  |                                       |  |
| FMAM2101          | Quality cont  | rol sample at mid level - for a | AMoN (NH <sub>4</sub> only no PO <sub>4</sub> ) - | Round to 3 decimal places using ev  | en/odd rounding rules                 |  |
| _                 |               |                                 |   | FMDL Criteria is +/- 30% FCRM is +/   | - 15% but not 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

#### 14.3. Analytical Accuracy

As seen in **Table 19** many QC standards are analyzed with each batch of AMON and NTN samples. All of these QC standards can be viewed in the Benchem LIMS to assess issues with accuracy and potential bias. When bias is suspected all the standards and QC samples, (i.e. PTs) will be assessed for similar patterns. In order to demonstrate examples of accuracy assessment most of the following graphs **Figures 20 – 36** are for the faux rain water mix (FMDL) that is prepared in the lab from Type I water and clean spikes at

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concentrations of approximately 2-10 times the MDL level. In some cases low or mid-level standards are also displayed as indicated in the titles. The y-axes are in units of concentration for each graph.



#### Figure 20. Calcium FMDL 2001 solution recoveries.



Figure 21. Potassium FMDL 2001 solution recoveries.



Figure 22. Sodium FMDL 2001 solution recoveries.

|              |        |            |        |      |           |           |          |         |       |             | Date range | ;        |         |           | 1       | Filters       |        |        |
|--------------|--------|------------|--------|------|-----------|-----------|----------|---------|-------|-------------|------------|----------|---------|-----------|---------|---------------|--------|--------|
| Туре         | QC     |            | $\sim$ |      |           | Sample ID | FMDL2001 | ~       | Start | Wednesday,  | January    | 1, 2020  |         | Analyst   | blaydek | n             |        | $\sim$ |
| QC Project   | Lab QC | ;          |        |      | $\sim$    | Analyte   | Mg       | ~       | End   | Thursday ,  | December   | 31, 2020 | -       | 🗌 Inst ID | ICP     |               | el ICP | $\sim$ |
| Control Char | t      |            |        |      |           |           |          |         |       |             |            |          |         |           |         |               |        |        |
| 0.           | 025    |            |        |      |           |           |          |         |       |             |            |          |         |           |         |               |        |        |
|              | 0.02—  | -          |        |      |           |           |          |         |       |             |            |          |         |           |         |               |        |        |
| 0.           | .015 - |            |        |      |           |           |          |         |       | ~           |            |          |         |           |         |               |        |        |
|              | 0.01-  |            |        |      | ~~~       |           |          |         |       |             |            |          |         |           |         |               |        |        |
| 0.           | 005    | 02/01/20 ( | 00:00  | 03/0 | 1/20 00:0 | 0         | 04/01/2  | 0 00:00 |       | 05/01/20 00 | D:00       |          | 06/01/2 | 0 00:00   |         | 07/01/20 00:0 | 0      |        |

Figure 23. Magnesium FMDL 2001 solution recoveries.



**Figure 24.** Ammonium – AMoN and NTN FIA - FMDL 2001 solution recoveries. All the QC exceedances were observed on the AMoN Lachat. Eventually the Lachat tubes used for AMoN QC samples only (samples are in Radiello tubes) were found to have sporadic NH4 contamination affecting QC checks such as FMDL and preparation blanks. Radiellos have not shown any contamination and are always used for samples. As seen in **Figure 25**, the problem was resolved with all Radiellos on 8/11/2020.



Figure 25. Ammonium recoveries after tube change in August 2020 and fresh MDL standard (FMDL2002).



#### Figure 26. Ortho phosphate FMDL 2002 solution recoveries.



**Figure 27.** Chloride FMDL 2002 solution recoveries. This shows potential low bias but this is an in-house prepared standard mix so the standard may have been prepared slightly too low – therefore the low-level standard recoveries are assessed in **Figure 28**.

|              |        |                |            |           |             |        |       | Date range                     |                             | Filters          |             |
|--------------|--------|----------------|------------|-----------|-------------|--------|-------|--------------------------------|-----------------------------|------------------|-------------|
| Туре         | QC     | ~              |            | Sample ID | FL190001    | $\sim$ | Start | Wednesday, January 1, 2020 🗐   | - Analyst                   | cw               | ~           |
| QC Project   | Lab QC |                | $\sim$     | Analyte   | CL          | $\sim$ | End   | Thursday , December 31, 2020 🗐 | <ul> <li>Inst ID</li> </ul> | NADP_ir ~ 🗌 Char | nnel NADP ~ |
| Control Char | t      |                |            |           |             |        |       |                                |                             |                  |             |
| 0.           | 035    |                |            |           |             |        |       |                                |                             |                  |             |
| (            | 0.03-  |                |            |           |             |        |       |                                |                             |                  |             |
| 0.           | 025    | A martine      |            | y ferman  |             | ~~~    |       | - Any - Ange - pr              | kalaanalaana                | 1 11-A hours     |             |
| (            | 0.02-  |                |            |           |             |        |       |                                |                             |                  |             |
| 0.           | 015 -  |                |            |           |             |        |       |                                |                             |                  |             |
| (            | 0.01-  |                |            |           |             |        |       |                                |                             |                  |             |
| 0.           | .005   | 02/01/20 00:00 | 04/01/20 0 | 0:00      | 06/01/20 00 | 0:00   |       | 08/01/20 00:00 10              | /01/20 00:00                | 12/01/20 00:0    | 00          |

**Figure 28.** Chloride low level standard (FL) recoveries. This shows excellent precision and accuracy with only one outlier.

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**Figure 29.** Sulfate FMDL 2002 solution recoveries. This shows potential low bias but this is an in-house prepared standard mix so the standard may have been prepared slightly low – therefore the low level standard recoveries are assessed in **Figure 30**.



**Figure 30.** Sulfate low-level standard (FL) recoveries. This shows excellent precision and accuracy with only one outlier.



**Figure 31.** Nitrate FMDL 2002 solution recoveries. This shows potential low bias but this is an in-house prepared standard mix so the standard may have been prepared slightly too low – therefore the low-level standard recoveries are assessed in **Figure 32.** 

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**Figure 32.** Nitrate low-level standard (FL) recoveries. This shows excellent accuracy and precision with only one outlier.



Figure 33. pH low-level (FL) standard recoveries. Demonstrates slight high bias.



Figure 34. pH mid-level (FM) standard recoveries.

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Figure 35. Conductivity low level (FL) standard recoveries. Demonstrates slight low bias.



Figure 36. Conductivity mid-level (FM) standard recoveries.

### 15. NTN Supply QC

#### 15.1. NTN Supply QC

Each network within the NADP long-term monitoring program requires very specific sampling and processing supplies, which are all cleaned and prepared using established specialized protocols to maintain data consistency throughout the networks. The CAL must supply materials of identical quality to those being replaced at the sites. The laboratory cleans and provides supplies for NTN and AMoN. In order to verify that supplies are adequately clean, supply blanks are measured as outlined in **Table 20** and **Table 22**.

### 15.2. New Supply Assessment

New lots of NTN bottles, ICP/FIA test tubes, filters, and bucket sampling bags that are not routinely prewashed must meet established "Lot QC" based criteria before use within the networks. Details are provided in NADP SOP 200 "NTN and MDN Supply QC" – a brief summary is provided below.

New Filter Lot Testing

All viable NTN samples are filtered upon receipt. Polyethersulfone 0.45 µm filters are used to isolate the insoluble particulate matter from the operationally defined soluble/dissolved fraction in all NTN precipitation

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samples. Extractable contaminants in these filters are assessed with each new filter lot prior to use and additionally with one filter at the start/end of each filter day and weekly syringe filter blanks.

## 15.3. New Bottle, Bag and Test Tube Testing

<u>New</u> bottles, sampling bags and test tubes are <u>lot tested</u> prior to use per the protocols in **Table 20**.

| ltem                      | Solution   | Amount &<br>Frequency               | Project LOG IN                | Client<br>Number                     | LIMS Description   |
|---------------------------|------------|-------------------------------------|-------------------------------|--------------------------------------|--|
| BAG LOTS                  |            |                                     |                               |                                      |  |
| NTN Sample Bags           | ~150 mL MQ | 20/new lot<br>(unless <500 then 10) | New Sampling Bag<br>Lot Check | Date Prepared &<br>Preparer Initials | Bag Type, Lot #, Bag#<br>(i.e. NTN Sample Bag Lot X 1of20)                     |
| NTN Bucket or Lid<br>Bags | ~150 mL MQ | 5/new lot                           | Bag Blank Study               | Date Prepared & Preparer Initials    | Bag Type, Lot #, Bag#<br>(i.e. NTN Bucket Bag Lot X 1of5)                      |
| BOTTLE LOTS               |            |                                     |                               |                                      |  |
| NTN 60mL HDPE<br>Bottles  | ~60mL MQ   | 10/new lot<br>(unless <100 then 5)  | NADP New Bottle<br>Blanks     | Date Prepared &<br>Preparer Initials | Bottle Type, Lot #, Bottle#<br>(i.e. 60mL NTN LotX 1of10)                      |
| NTN 1 Liter HDPE<br>(New) | ~150 mL MQ | 10/new lot<br>(unless <100 then 5)  | NADP New Bottle<br>Blanks     | Date Prepared & Preparer Initials    | Bottle Type, Lot #, Bottle#<br>(i.e. 1L NTN LotX 1of10)                        |
| FILTER LOTS               |            |                                     |                               |                                      |  |
| NTN 47mm Disc<br>Filters  | 60 mL MQ   | 20/New Lot<br>min 2 boxes from lot  | Filter Blank Lot<br>Testing   | Date Prepared & Preparer Initials    | Lot, Box#, Filter #, Brand, filter type  |
| NTN Syringe Filters       | 20 mL MQ   | 5 per lot of 150                    | Filter Blank Lot<br>Testing   | Date Prepared & Preparer Initials    | Lot, Box#, Filter #, Brand, filter type  |
| TUBE LOTS                 |            |                                     |                               |                                      |  |
| NTN Test Tubes            | 2-10 mL MQ | 10/New Lot ICP/FIA                  | Test Tube QC Blank            | Date Prepared &<br>Preparer Initials | Brand, Test tube type, lot # & tube #<br>(i.e. Fisher, ICP, Lot 3434, 2 of 10) |

### 15.4. Lot Testing Criteria

The CAL lot testing criteria states that the mean of at least 10 samples per lot must be < NTN MDL<sub>N</sub> and none of the supply blanks in the batch tested may exceed 3 times the NTN MDL<sub>N</sub> for any analyte the supply is used for (for HAL supplies we only assess total mercury for example). If the criteria are met, the new lot can be used. If the QC criteria are not met then another set of 10 must be tested or the entire lot is rejected and returned to manufacturer. If the second test fails, the lot must be rejected. For lots of filter or bag supplies greater than 1000 a minimum sample set of 20 QC checks are analyzed. Lot protocols are listed in **Table 20**, and results for the numbers of samples in 2020 are shown in **Table 23**.

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| Item tested              | # of 2020 QC<br>Samples | Number<br>Individual<br>Samples Failed | Lots Tested | Lots Rejected | Lots Approved |
|--------------------------|-------------------------|--|-------------|---------------|---------------|
| Bottles - 60 mL and 1 L  | 100                     | 0                                      | 10          | 0             | 10            |
| Large NTN Disk Filters   | 58                      | 1                                      | 2           | 0             | 2             |
| Syringe Filter           | 45                      | 4                                      | 5           | 0             | 5             |
| Syringes Only            | 40                      | 3                                      | 5           | 0             | 5             |
| Test Tubes - ICP and FIA | 104                     | 0                                      | 10          | 0             | 10            |
| Total                    | 347                     | 8                                      | 32          | 0             | 32            |

### 15.5. Ongoing Supply Assessment

Data from the ongoing supply QC program (**Table 22**) is assessed, at a minimum, on a quarterly basis. Trends in potential contamination or supply issues are investigated and corrective action taken as needed. Analysts are to notify the QA Manager if they notice high supply blanks in analytical runs so that they can be followed up on as quickly as possible. Reused (or new washed) NTN supplies are assessed for blank values above the supply criteria which are set to the NTN MDL<sub>N</sub>. Results for 2020 ongoing supply QC testing are shown in **Table 23** and **Figure 37**. Overall, these data demonstrate that cleaning and supply/lot protocols are clearly in control, with remarkably few exceedances.

Table 22. Ongoing Supply QC Types and Frequency (NTN)

| ltem                               | Project Log In              | Amount/Frequency     | Solution   | LIMS Description   |
|------------------------------------|-----------------------------|----------------------|------------|--|
| TYPE I WATER                       |                             |                      |            |  |
| NTN Type 1 H <sub>2</sub> O Blanks | MQ Water System Blanks      | 1/purifier/week      | 60 mL MQ   | "Type 1 Water Blank", BLDG, Lab #<br>(i.e. Type 1 Blank, AG 200B, HM135) |
| NTN SUPPLIES                       |                             |                      |            |  |
| NTN 47mm Disc Filters              | Filter Blanks DI            | 2/ Filter Day        | 60 mL MQ   | "Start/End Filter" & Sample Range  |
| NTN Syringe Filters                | Weekly Syringe Filter Blank | 1 per week           | 20 mL MQ   | "Syringe Filter Blank", Syringe and<br>Filter Lot#                       |
| NTN Sample Bags                    | Bag Blank Study             | 1/week               | ~150 mL MQ | Bag Type, Lot#   |
| NTN 1 Liter HDPE                   | Bottle Blanks               | 1/wash day           | ~150 mL MQ | "1L NTN Washed"  |
| NTN Buckets                        | Bucket Blanks               | 1/wash day           | ~150 mL MQ | "New" or "Used" "Bucket"   |
| NTN LIDS                           | Lid Blanks                  | 1/wash day /per type | ~100 mL MQ | Lid Type   |

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#### Table 23. NTN Ongoing Supply QC Exceedances

| Item Tested             | Са | Na | К | Mg | Cl | SO <sub>4</sub> | NO <sub>3</sub> | NH <sub>4</sub> | PO <sub>4</sub> |
|-------------------------|----|----|---|----|----|-----------------|-----------------|-----------------|-----------------|
| Used 1L Bottles (n=200) | 0  | 0  | 0 | 0  | 0  | 0               | 0               | 0               | 0               |
| Used Buckets (n=196)    | 0  | 0  | 0 | 0  | 0  | 0               | 3               | 5               | 0               |
| New Buckets (n=11)      | 0  | 0  | 0 | 0  | 0  | 0               | 0               | 0               | 0               |
| Bags(n=20)              | 0  | 0  | 0 | 0  | 0  | 0               | 0               | 0               | 0               |
| Used Lids (n=405)       | 3  | 2  | 2 | 0  | 8  | 0               | 1               | 2               | 0               |
| New Lids (n=14)         | 0  | 0  | 0 | 0  | 1  | 0               | 0               | 0               | 0               |
| MQ H20 (n=260)          | 0  | 0  | 5 | 0  | 1  | 2               | 3               | 5               | 14              |
| Disc Filters (n=364)    | 0  | 2  | 2 | 0  | 1  | 0               | 0               | 0               | 0               |
| Syringe Filters (n=53)  | 0  | 0  | 0 | 0  | 7  | 0               | 0               | 0               | 0               |



**Figure 37.** Percent of 2020 Ongoing Supply QC Tests that Exceeded NTN Network MDLs (no exceedances for used 1 L bottles, bags, and new buckets).

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### 16. AMoN Supply QC

Atmospheric ammonia sampling is performed using Passive Diffusion Samplers (PDS) approved by NADP (currently restricted to Radiello<sup>®</sup> products). These samplers and associated shipping supplies undergo extensive cleaning and validation practices. A variety of QC samples are tested to ensure background ammonia remains low in all prepared supplies as well as the preparation and extraction environment.

As outlined in **Table 24**, "AMoN Supply QC", the diffusive bodies and cores are "blank" tested as well as the glass storage/shipping jars, extraction water and various hood/room blanks from the laboratory AMoN processing suite.

| Item                               | Solution               | Amount & Frequency                           |
|------------------------------------|------------------------|--|
| Jars                               |                        |  |
| Glass Jar – NEW                    | 10 mL MQ               | 1/wash batch                                 |
| Glass Jar – USED                   | 10 mL MQ               | 1/wash batch                                 |
| Blanks With Cores                  |                        |  |
| Core Blanks                        | 10 mL MQ               | 2 per NEW lot (only for new lots on arrival) |
| Prep Blanks (body+core+jar)        | 10 mL MQ               | 1/sampler prep batch per sonicator           |
| Water Only Blanks                  |                        |  |
| Sonicator Blank                    | 10 mL Sonicator $H_2O$ | 1/sampler prep batch at end of prep          |
| Method Blank<br>(extraction water) | 10 mL MQ               | 1/extraction day                             |
| Hood/Room Blanks                   |                        |  |
| 2 Week Air Blank Sonicator Hood    | 10 mL MQ               | 1/two week period                            |
| 2 Week Air Blank Extraction Hood   | 10 mL MQ               | 1/two week period                            |

Table 24. AMoN Supply Quality Control 2020

Each preparation week a number of AMoN QC samples are also prepared and tested to monitor potential background contamination. There were slightly more exceedances in the 2020 but the majority of those were jar and water blanks. The most significant indicator of overall cleanliness are the preparation blanks and none of those exceeded criteria. All details are provided in **Table 25**.

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|                        | 2019 MEAN | 2020 MEAN | 2019 # TESTED | 2020 # TESTED | Number of<br>exceedances | Number of<br>exceedances | Criteria                   |
|------------------------|-----------|-----------|---------------|---------------|--------------------------|--------------------------|----------------------------|
| Preparation Blanks     | 0.013     | 0.006     | 99            | 69            | 0                        | 0                        | 0.037 mg/L NH <sub>4</sub> |
| Core Blanks            | 0.010     | 0.005     | 73            | 74            | 1                        | 2                        | 0.037 mg/L NH <sub>4</sub> |
| 2 Week Hood Blanks     | 0.051     | 0.070     | 52            | 50            | 0                        | 0                        | 0.4 mg/L NH <sub>4</sub>   |
| Room Blanks            | 0.510     | 0.749     | 25            | 27            | 0                        | 1                        | 1.2 mg/L NH <sub>4</sub>   |
| Hood Extraction Blanks | 0.017     | 0.010     | 51            | 54            | 0                        | 0                        | $0.2 \text{ mg/L NH}_4$    |
| Water Blanks           | 0.002     | 0.002     | 171           | 164           | 0                        | 5                        | 0.013 mg/L NH <sub>4</sub> |
| Jar Blanks             | 0.003     | 0.003     | 112           | 120           | 1                        | 6                        | 0.013 mg/L NH <sub>4</sub> |
| Total                  |           |           | 583           | 558           | 2                        | 14                       |                            |
|                        |           |           |               |               | 2019 % Excee             | dance                    | 0.3                        |
|                        |           |           |               |               | 2020 % Excee             | dance                    | 2.5                        |

## Table 25. AMoN Supply QC Summary 2019-2020 and results in mg/L NH<sub>4</sub>

#### 17. Occurrence Management

The CAL uses a WSLH lab-wide reporting system to record all major deviations from standard protocol, reoccurring issues and corrective actions. Occurrences are reviewed bimonthly at staff meetings and corrective actions are detailed, implemented and verified before occurrences can be closed out. Occurrence management is a tool to help track issues, identify trends, implement changes and educate staff on common problems. Details from 2020 can be viewed in the Annual Management Review section above. A summary of metrics is provided in **Table 26**.

Table 26. Summary of Occurrences 2020

| Number of Recorded CAL<br>Occurrences | Category of Issue               |
|---------------------------------------|---------------------------------|
| 2                                     | Recording Major Protocol Change |
| 6                                     | Sample Handling                 |
| 4                                     | Analytical QC                   |
| 1                                     | Supply QC                       |
| 13                                    | Total                           |

### **18. Method Improvement Projects**

The NADP Lab has continued to test and assess new techniques and supplies that might improve outcomes and efficiencies of the networks. Some of the initiatives pursued in 2020 include:

- Implementation of NTN sample bags (reduction in costs for shipping, bucket washing)
- Test dip coating of phosphoric acid onto used AMoN cores (potential cost savings)
- Began exploring recycling options for gloves and bags

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- Extended NTN ammonium calibration curve (reduce number of sample dilutions)
- Transitioned from AMoN field triplicates to duplicates
- Comparison study of white vs. blue AMoN diffusion bodies (a peer-reviewed paper had noted a potential difference in ammonia results)
- Extended NTN ammonium and ortho-phosphorus reagent holding times from 1 week to 3 weeks
- Ongoing five-year archive preservation study (112 samples preserved frozen and refrigerated)
- Fall 2020 NADP conference scientific symposium discussed formaldehyde-(bi)sulfite (hydroxymethanesulfonate (*HMS*)) as a possible interference with sulfate (false positive). We tested and found no interference issues
- Integrated our CAL "possible data qualifier spreadsheet" into the data review process/assessment

### 19. Special Studies

The NADP mission includes efforts to maximize the scientific impact of the network infrastructure and analytical capabilities at the WSLH. It is through these studies that the NADP program will ultimately grow and continue to be relevant. The primary vehicle through which this mission goal is being addressed is via special studies with either external or internal scientists. Special studies are required to go through a rigorous multi-step approval process at the CAL and PO. This begins with the completion of an official request form and review by PO and CAL. If approved, the requested NADP samples can be used for the research project. It is the goal of the CAL/PO review to provide constructive feedback to the researcher to improve the study outcomes. Special Studies that were in-place or implemented in 2020 are shown in **Table 27**. Fees are incurred for special study requests and NADP data needs are always the first priority.

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| Table 27. NADP Samples Provided to Outside Research | Groups (all for NTN) January 2020 through |
|---|---|
| December 2020.                                      |   |

| Cooperator and<br>Affiliation   | Network      | # of Samples<br>Provided                           | Notes   |
|---|--------------|--|---|
| Greg Wetherbee<br>(USGS)<br>Richard Dabundo (Univ.<br>Pittsburgh)<br>Sheila Murphy (USGS) | NTN          | 27 filtered<br>water samples                       | Water samples analyzed for stable isotopes; filters analyzed for urban pollution tracers.   |
| David Clow (USGS)   | NTN          | 32 filtered water samples                          | Estimate water residence times in the Loch Vale research watershed.   |
| Ty Coplen (USGS)  | NTN          | 279 filtered water samples                         | Measure stable hydrogen and oxygen isotopic abundances to generate a historic time line of these data in the subject area.  |
| Jessica Conroy (Univ. of<br>Illinois)   | NTN          | 255 filtered water samples                         | Investigate controls on the stable isotopic composition of North<br>American mid-continent rainfall on weekly timescales.   |
| Monica Ramirez-<br>Andreotta (Univ. of<br>Arizona)  | NTN          | 49 unfiltered<br>water samples                     | Samples will be analyzed to compare results from sample collected from rooftop systems for home agriculture purposes.   |
| Drew Spear/Stephen<br>Monroe<br>(Mesa Verde National Park)                                | NTN          | 43 filtered water samples                          | Develop a conceptual model of GW flow and potential vulnerability of selected springs to effects of climate change or anthropogenic contamination including WW/runoff from developed areas in park. |
| Janice Brahney (Utah<br>State Univ)   | NTN          | 135 filters &<br>unfiltered water<br>samples       | The purpose of this special study is to determine if NADP NTN can be used to monitor for virus presence in the atmosphere.  |
| Martin Shafer (WSLH)<br>and WDNR  | NTN          | 117 unfiltered water samples                       | PFAS in precipitation.  |
| Phil Silva/Mike Bryant<br>(Western KY University)   | AMoN/<br>NTN | 22 AMoN<br>extracts &<br>filtered water<br>samples | This study aims to determine whether organic nitrogen (amine) speciation and quantification can be obtained from the AMoN network.  |
| Eric Oseland (University of Missouri)   | NTN          | 10 filtered water samples                          | Our objective is to measure levels of dicamba found in deposition prior to and after dicamba tolerant soybeans were released in several geographically distinct regions of the United States.       |
| James Ranville<br>(Colorado School of<br>Mines)   | NTN          | 8 unfiltered water samples                         | Determine the nature of nanoparticulate and colloidal particles<br>in rainwater and examine urban and wildfire influences.  |
| Carl Bern (USGS)  | NTN          | 194 filtered water samples                         | To use the isotopic composition of water (180 and 2H) from precipitation and surface water to better understand the controls on water availability in the Upper Colorado River Basin.               |
| Alexandra Ponette-<br>Gonzalez (University of<br>North Texas)                             | NTN          | 64 filters and filtered water samples              | The goal of this study is to investigate the chemical and<br>elemental fingerprints of large wildfires in rainwater and to<br>quantify associated wet deposition fluxes.                            |
| Ross Edwards (UW<br>Madison)  | NTN          | 655 unfiltered water samples                       | Black carbon analysis and deposition. A synoptic overview across USA  |
| EPA/Wood Env  | NTN          | 71 unfiltered<br>water samples                     | PFAS in precipitation.  |

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#### 20. Data Review

#### 20.1. Analytical Data Review

There are several steps to ensure that data are accurate and properly qualified before moving to the data review stage. These include:

- a. Peer review a second analyst reviews all data packets prior to results being uploaded to the NADP LIMS and released to the sites in monthly reports.
- A pH and conductivity QC review secondary QC review of pH and conductivity packets and QC due to the automatic upload of instrument data to the Laboratory Information Management System (LIMS) at the time of analysis.
- c. Possible Qualifiers spreadsheet record of all anomalies with samples during preparation/analysis.
- d. Duplicate failures spreadsheet record of all duplicate failures even those corrected by rerun to assess trends.
- e. LIMS Compare monthly data packet review per platform compared to LIMS analytical data. Extra checks on duplicates and dilutions.

### 20.2. Network Data review

Prior to releasing reports to sites or publishing data to the PO, the CAL or HAL reviews all NADP sample data for completeness and consistency. This includes comparison to historical site values, precipitation review, second data entry and review of possible analytical qualifiers.

### 21. Data Management review

NTN and AMoN samples are all analyzed within target holding times (3 weeks from receipt for NTN and 3 weeks from date off for AMoN), and data are peer reviewed within 1-3 weeks of analysis and then uploaded to the NADP LIMS. Therefore, most data are uploaded to the NADP LIMS within 4 weeks of sample receipt. CAL data turnaround time is calculated from the end of the month in which a sample was received to when the data were reported to the site and published to the PO. Publishing on the website is the responsibility of the PO. COVID-19 impacts on personnel resources and the integration of the MDN and its new LIMS system for this network complicated 2020. Resources were moved temporarily to help with this process, which delayed data review for NTN and AMON. However, there was still a downward turnaround time (TAT) trend during 2020 and in early 2021 our TAT's have come down to 90 days and are holding steady. This improvement resulted from the completion of the MDN integration (moving resources back) and changing from a linear data review approach to a multi-faceted parallel approach. Refer to **Figure 38** for Data Review TATs.



**Figure 38.** WSLH CAL Data Deliverables: Preliminary Reports to Sites and Data Delivered to the NADP Program Office by Network as of Month Year. Note: 90 days is our target TAT.

### 22. References

- National Atmospheric Deposition Program Laboratory Quality Assurance Plan, Mercury and Central Analytical Laboratories. Revision 1, June 25, 2020 (<u>http://nadp.slh.wisc.edu/lib/qaPlans.aspx</u>
- Wetherbee, G.A., and Martin, RoseAnn, 2020, External quality assurance project report for the National Atmospheric Deposition Program's National Trends Network and Mercury Deposition Network, 2017– 18: U.S. Geological Survey Scientific Investigations Report 2020-5084

### 23. Approvals

- 2020 CAL QAR Prepared by Chris Worley CAL Manager, Camille Danielson, NADP CAL/HAL QA Manager and Data Processing Manager Amy Mager Completed Draft: 8/31/21
- Shared with External Review Team, PO and NADP Management as Draft on: 8/31/21
- Approved by the NADP Program Office Mark Olson: 9/3/21
- Reviewed and revised by Systems QA and Special Projects Manager Martin Shafer: 9/12/21
- Shared with the QAAG for review on: 9/29/21
- Approved by QAAG by vote: 10/19/21
- Announced at Fall 2021 Technical Conference