National Atmospheric Deposition Program (NADP)
Quality Assurance Advisory Group (QAAG)
Meeting: April 22, 2021
Co-chairs: Martin Shafer, Camille Danielson
Minutes by: Camille Danielson

NADP QAAG Minutes
Thursday April 22nd
2:00 PM – 3:30 PM CDT

Members Present: Camille Danielson, Martin Shafer, Mark Olson, Chris Worley, Amy Mager, Richard Tanabe, Bob Larson, Zac Najacht, Dana Grabowski, Na Zhang, Greg Wetherbee, Eric Hebert, Maria Jones, Tim Sharac, Melissa Puchalski, Greg Beachley, Cheryl Sue, Marcus Stewart, Winston Luke, Jason O'Brien

Items for Discussion

1. New Member! Jason O'Brien (currently the acting Head of CAPMoN but his substantive job is related to the nitrogen science and guest Michael Harwood the ECCC Field Lead
2. Site Support Issues/Questions – EEMS/PO
    - AMoN meteorological conditions during the "period". Should that be the time of installation or the entire two-week period? Eric said some operators don't know how to use this.
        - Richard clarified that if the operator had knowledge of the entire time period conditions they could check all that apply otherwise should leave blank.
        - Camille Noted that leaf cover and weather are not entered into CAL LIMS – so no capture of this data– should we remove from forms or start to capture?
        - Some discussion of the history and use of the data but not clear if anyone is using it
    - Is the frog deterrent covering the gage approved? Eric showed picture of homemade frog screen over rain gage covered in bird droppings.
        - If so can we improve the design to make it a easily removable cover and use it at other sites? Should we do a comparison to see if it is bias low when used?
        - Some concern over bias caused by this gage, discussion of the frog problem being limited to a few sites most in FL.
        - Greg found a spike ring that might be able to be put on the rain gage – but this also would need to be tested.
        - Dana reported that she has a way of telling from the gage records when there is a frog issue and she can adjust the precipitation.
    - Is there any approved wasp spray for AMoN, MDN, or NTN?
        - Not that anyone was aware of – Greg said we would look into ingredients and find a solution.
    - Update on Site Audits
        - Site audits on schedule except Canada and Alaska due to Covid limitations.
3. Siting Criteria Update - Tim Sharac
    - Tim gave a detailed presentation available for separate review
    - Key points:
    - The primary factors contributing to siting criteria violations include
        - "No objects >1m tall w/in 5 m" (45.2%)
        - "No vegetation > 0.6 m tall w/in 5 m" (23.8%)
        - "Dry side bucket is clean" (22.2%)
        - **Overall 24% of sites met all siting criteria**
    - A strategy to determine the data quality impacts:
        - What are the trends in siting criteria violations?
        - What are the trends for NTN QR codes?

- What is the relationship between NTN debris codes
- What are the trends for NTN debris counts?
- Create list of NTN site pairs within 50 km apart
- What are the trends in siting criteria violations at NTN pairs?
- Compare debris type and quantity between NTN site pairs
- Next steps – decided that the workgroup needed to get back together to further discuss the best approach to improving the siting criteria

4. Methyl Mercury (Christa CZD)
   - 122 samples have been analyzed at HAL since WSLH took over
   - 4 out of 122 have been above the detection limit of 0.1 ng/L.
   - All were less than 0.2 ng/L (LOQ=0.33 ng/L)
   - In 3 of those samples, at least one component of the composite was given a debris note.
   - The one sample with no debris note was measured at 0.10 ng/L
   - Debris/contamination notes are only recorded if it was reported by the site operator. The lab regularly receives samples which appear to contain contamination which was not reported by the operator. This gets recorded as a sample qualifier.
   - 27 composite samples were created and tracked that ultimately contained insufficient volume (<30 mL) to be analyzed.
   - Methylmercury in precipitation is largely not detectable. When detectable, it is challenging to determine if the methylmercury was:
   - Deposited as methylmercury OR
   - Contaminated by mishandling, debris, insects, etc.
   - In either case, biotic alkylation of inorganic mercury in the environment after deposition should quickly outpace direct deposition of methylmercury.
   - WSLH Recommendation
     - Discontinue analysis of methylmercury in precipitation except for special projects. The method will be maintained by WSLH in order to support surface water monitoring programs.
     - Stop compositing samples. Methylmercury will be analyzed from individual samples with a volume greater than 200 mL (aliquot collected before bromination for total Hg). This could either include or exclude debris/contamination samples.
5. DQO Update – Martin et al Creating DQO workgroups
   - **Data Quality Objectives (DQO) Workgroups**

   A. Trend Measurement/Detection
   a. Both spatial and temporal
   b. Statistical tools and metrics
   c. Summarize historic/current efforts with national monitoring network data
   d. How are data uncertainties captured in the trend analyses?
   e. Guidance for integration into DQOs
   f. 5 + Participants

   B. Data Completeness
   a. Critical examination of criteria rationale
   b. Critical examination of decision rules
   c. Guidance for improved integration into DQOs

d. Integrate findings with those from Trend Measurement team
e. 5+ Participants

C. Deposition/Precipitation

a. Uncertainty focus
b. Measurement-Model Fusion
c. Mapping criteria
d. PRISM versus site specific e-gage uncertainties
e. 5+ Participants

D. Overall Network Uncertainties

a. Summarize what we've learned from existing data
b. Focus on co-location data (or equivalent) – all analytes
   i. NTN – colocation program
   ii. MDN – colocation study (do we need an ongoing program?)
   iii. AMoN -- triplicates
c. Vision for future assessments
d. Guidance for setting rationale DQOs
e. 5+ Participants

E. Parsed/Component Network Uncertainties

a. Examine major laboratory and field uncertainty components
b. Use existing QA/QC sample data
c. Guidance for effort direction where improvements in network performance are under consideration (with DQO goals)
d. 5+ Participants

6. Data Review Metrics Reports/"q" notes code (Amy et al)
   - We have had OIS create custom queries in our LIMS so we can pull metrics more easily.
   - A q notes code has been created for NTN and AMoN to indicate a minor QC issue with a sample – to start using to flag data with Jan 2021
7. Comparison of NTN analytical chemistry data to site historical data for determination of sample validity (Zac et al)

NTN analytical chemistry data to site historical data for determination of sample validity

- General description of relationship of visible debris contamination, analytical data comparison to site history, and overall sample validity
  - Sample validity is determined, in part, based on the presence of visible debris in sample in combination with comparison of the individual analytical chemistry data to site historical values
  - Individual analytes, as well as pH and Conductivity values that are on the high or low end of the historical averages are scored - Screening Level (SL Coding)
    - These scores are totaled and the composite sum represents a sample's total "SL score"
    - SL scores of 4.0 or higher, in combination with certain visible debris present in sample, prompts an SL score of "C" resulting in a QR=C (invalid sample)
    - SL scoring table:

Concentration vs Site History	pH & Conductivity	All Other Analytes
> Maximum	1	2
≥ 90th percentile & ≤ maximum	0.5	1
≤ 10th percentile & ≥ minimum	0.5	0
< Minimum	1	0

- A composite SL Score is generated for every sample by an automated compilation of all individual analyte SL scores

Analytical Chemistry Data:

- Current criteria and method for coding/determining sample validity based on contamination & analytical chemistry data comparison
  - Two categories
    - New sites
      - 10 samples that are not "grossly contaminated"
        - This approach greatly limits the historical comparison consistency and accuracy & could vary greatly site to site
        - Looking at only 10 samples may lead to a high probability of a new maximum being achieved, and the sample being invalidated
          - i.e. One site may be considered established after 10 weeks, while another may take months.
      - After these 10 samples are submitted, reviewed and validated site is considered "established" and historical chemistry data comparison & visible debris in the sample are then used in determination of sample validity.
    - Established sites
      - Complete site history used for comparison (no matter how long the site has been in operation)
        - Validation inconsistency leading to site trends being misrepresented, overlooked or incomplete
- Proposed new criteria
  - New sites
    - One year of sampling/submitting from site before site is considered established & chem data historical comparison used for validity determinations
    - Samples not invalidated due to site history until after this one year period
    - Use same SL scoring/coding metrics
  - Established sites
    - Use same SL scoring/coding metrics
    - Complete site history not used for comparison, suggest capping off at the most recent 10 years
    - Sample historical comparison for validity would begin after first complete year and only use up to 10 years data maximum
- **Data Review Motion:**
  For new NTN sites, do not use historical chemistry data comparison for determination of sample validity until the site has completed one year of sampling and is considered established.
  For established sites that have completed one year of sampling, limit historical comparison to ten most recent years of the site's analytical chemistry data

This was all discussed and decided the motion should be brought to NOS at the Spring Conference for a motion/discussion

8. Virtual Lab Reviews, Who, What, How, and When? Greg Wetherbee and Richard Tanabe –
    - Greg W, Cheryl Sue, Emmi Felker-Quinn, Tim Sharac, Melissa Puchalski, Chris Rogers
    - Late August/Early September
    - Virtual review of PO, CAL, HAL working with Richard Tanabe and Camille Danielson
    - New procedure to share with QAAG for approval
        - Take some selected data back through the process
9. USGS Precipitation Chemistry QA Project GW
    a. 2020 Interlab data are incomplete and highly variable - preliminary control charts were reviewed and will be presented at Spring Conference
        a. Some issues with samples and results over the year of Covid. Some Hg samples appeared to not be stable. Low 0.1 ng/L bias seen in the HAL samples from WSLH.

    b. Discuss moving sample preparation and shipping to CAL/HAL in FY22? This was not discussed due to lack of time
10. Lab Investigation Projects – CAW
    - Blue and white AMoN Bodies
    - Core prep in-house
    - TN TP testing
11. Field QA – MLO/MS
    - Hg Field QA plan update (MO/MS)
        - Open collector study has been completed
        - 28 day Stability study will be complete on April 27, pH will be checked
        - pH is about 2.7 on full MDN samples
        - Duplicate samples have continued at Devils Lake
        - Spike samples will resume at the Arboretum
12. PFAS Field QA plan update (MO/MS)
    - Lid experiment is complete, used actual lids from ME96, NC30, WI06 and WI31 plus PFAS free. 7 days
    - VINs bags have been blank (3) and spike (3) tested over 7 days
13. Eagle Heights and Arboretum sample catch and exposure study has been initiated,
    - WI93 = NCon x2, ACM and KJJ
    - WI06 = NCon x 2 with slaved sensor
14. Lab QA Update CGD
    - New MDLs – we have new NTN and AMoN MDLs for 2021 data – will be presented at Spring Conference
    - Lid QC – some issues with lids contaminated with Ca or Cl primarily – eventually we traced back to construction being likely cause
    - pH Stirring
        - starting May 3 all pH sample stirred in test tube while being measured