

NADP Quality Assurance Advisory Group Meeting Minutes

March 4, 2019 12:30-3:00 CST

Attendees: Zac, Amy Mager, Richard Tanabe, Camille Danielson, Martin Shafer, Chris Worley, Mark Olson, Greg Wetherbee, Melissa Puchalski, Tim Sharac, Dave Wunderlich, Winston Luke, Michael Flournoy, Bob Larson, Marcus Stewart

Absent: Eric Hebert, Maria Jones

Camille called for changes, additions to QAAG membership roster, and none were suggested.

Greg Wetherbee volunteered to be QAAG secretary.

Action Items:

- ***Publish the RVP on the NADP web site as a .pdf file by Spring meeting (CGD/Bob)***
- ***Present motion to approve the OTT P2-S at the spring meeting (GW, MarkO, Bob L).***
- ***Recommend to Exec to remove the Br- data from the web and discontinue Br- analysis by June 2019 (MS/CGD).***
- ***Revise Bag sampling plan to incorporate comments from Melissa and Greg (RT).***
- ***Recommend to Exec to transition from bucket sampling to bag sampling consistent with the Bag Sampling Transition Plan (RT/MarkO).***
- ***CAL/PO to develop an official NADP procedure for editing of NADP databases where analytical values are changed (AM/ZN/BobL).***
- ***Add note to metadata file for AMoN indicating when acid matching of standards began. Include this information in the CAL QA Report (CGD/BobL)***
- ***Edit Archive plan to incorporate Melissa and Greg's written comments and to replace C000 with a different site in that region(CGD/RT/GW).***
- ***Package precipitation sensor data into an online data release (GW).***
- ***Find PTGE testing data and make it available to the CAL/PO (GW).***
- ***Methyl Hg sites to be contacted to see if they wish to continue testing (RT/MarkO).***
- ***Look into a process to reacquire old NADP equipment that is not being used – postpone until after HAL Transition (RT/MarkO).***

1. OLD Business

A. October 2018 QAAG Minutes: Greg moved to approve, Melissa seconded, minutes approved by acclamation as participation was less than exuberant.

B. October 2018 CAL RVP Report: Greg moved to have the RVP published on the NADP web site as a .pdf file by Spring meeting. Richard seconded, and motion carried.

C. HAL 2017 QAR: Report was reviewed by Mark Olson and Tim Sharac. Tim Sharac moved to approve, Greg seconded, approved unanimously.

D. Ott Pluvial S rain gage approval: OTT Pluvio2-S gage was not approved at fall 2017 meeting due to ongoing transition from Illinois to Wisconsin. OH16 has had a Pluvio2-S since November 29, 2017. Mark does not know where the comparison data are. Greg will look for them. Bob – Mark gave Greg data from IL11. Bob says P2-S is -4% compared to Pluvio2, especially due to light precip from smaller orifice. The second OTT P2-S at IL95 (i.e. IL11 sister site). Greg will work with Mark Olson and Bob L. and we'll try to make a motion to approve the OTT P2-S at the spring meeting.

2. NEW Business

A. Bromide Data Issues: Martin suggested that QAAG decide on these recommendations: 1. Pull Br- data off the web site, and 2. discontinue Br- analysis after 1 full year of WSLH-CAL measurements (June 2019). Winston asked Martin to briefly describe the issue to the group. Martin summarized the contents of his report that was made available to the group. Br- interference by oxalate was found by independent analysis using mass spectrometry. The method that WSLH obtained from PRI was consistent with the last 6 months of PRI Br- analysis. WSLH reran June-Sept. 2018 samples to get accurate Br- data, and only 2% of sample results were greater than the MDL. QAAG needs a recommendation before June on whether to continue the Br- analysis or not. As for the historic data on the NADP web site, a decision at the Albany meeting was made for Greg to lead an investigation of the PRI methodology. That investigation yielded some still unanswered questions related to database editing, updating, and transfer issues among others. WSLH looked at a selected set of samples, and about 25% of samples did not match the current database. Greg indicated that he is not comfortable with the PRI data, but there are undoubtedly some accurate data as well. The Br- data from PRI are questionable though. Greg explained that there are 2 journal articles and a Ph.D. dissertation that evaluated the data and that errata will have to be published for his article and a USGS data release. Greg moved to remove the Br- data from the web and discontinue Br- analysis by June 2019 as suggested by the CAL. Camille seconded, and the motion carried.

B. HAL (Transition) Lab Analytical Validation Plan: A validation plan was sent to QAAG members for review. Greg indicated that he did not think that it was within DOT regulations to ship brominated samples, and Michael Flournoy later confirmed this after consultation with Bob Brunette. Greg also cautioned about using natural matrix samples as previous use of them created a lot of variability in the interlaboratory-comparison, which Greg attributes (without solid proof) to particulate Hg in the natural matrix. Mark Olson moved to accept HAL RVP modified as needed to accommodate sample shipping regulations. Seconded by Camille. Unanimously approved.

C. NTN Bag Sampling: Bag sampling: Summary was sent to QAAG members for review on 2/5. Greg and Melissa sent written comments. Richard Tanabe discussed the plan as sent out to the QAAG along with changes of materials and equipment. Plan is to roll out bag sampling starting July 1, 2019 at 50 sites every 2 weeks and final change over by the fall meeting. Shipping options are being evaluated. This will make a huge difference in shipping costs by NTN. Preferred option is to ship 9 weeks of supplies,

possibly with poly liners for monthly shipping of dirty lids back to CAL. Discussion about reusing lids for the clean buckets and sample buckets ensued. QAAG did not have a problem with reusing the lid used to protect the bag to be transferred to the sample bucket at collection. Cheryl Sue pointed out that ECCC has seen some separation of the bags in summer due to heat. Richard moved to transition from bucket sampling to bag sampling consistent with the Bag Sampling Transition Plan provided to the QAAG. Greg seconded the motion. There was no discussion. Motion carried.

D. DMAG committee to be resurrected: Amy proposed to re-establish and re-energize the DMAG with members Bob Larson, Amy Mager, Zac Najacht, Casey Lanham, Chris Rogers, Kevin Mishoe.

E. NTN Coding Issues – Amy expressed the need to assess and improve coding and flagging options. LCC (lab contamination codes) were at issue at CO98 seeing higher frequency of contaminated sample flagging. CAL realized that samples coded with dirt/soot only should not be flagged as contaminated. This is important because SL-Coding program will flag sample as invalid if analyte concentrations are out of compliance along with observed contamination. Coding errors were discovered and corrected before data were published. CAL reissued reports for CO98, but not for any other sites. Changes for other sites were made by PO at the website level. Invalidated samples were revalidated as appropriate using the corrected flagging protocol for samples from June-September 2018. Data from October-December 2018 were also corrected before posting to the web. Greg mentioned that we should re-evaluate the 95th percentile concentration criteria to evaluate flagging as well. Zac thanked CO98 for bringing it to the CAL's attention.

F. Database editing: Amy indicated that CAL/PO will work on an official NADP procedure for editing of NADP databases where analytical values are changed. Camille suggested that is needed by June to accommodate Br- discontinuation.

G. AMoN Acid matching standards: Chris Worely indicated that the pH of the calibration standards are now being matched to field sample pH to improve NH₄⁺ detection. Color development is pH-dependent. Ran 80 samples against regular and acidified standards and a 0.04 mg/L bias was observed. So, WSLH is changing over to matrix matching of pH. Poster by N. Gartman indicated that changing the buffer was attempted at Illinois, but Illinois was not matrix matching. Cheryl Sue asked about the LACHET method that CAL is using. Extracted samples are at pH 2.2. This applies only to AMoN extracted cores, not precipitation samples. Melissa asked about documenting this change. Melissa suggested that a note on the metadata file would be appropriate. Martin indicated that it will be documented in the QA report.

H. AMoN Anti-static bag study: Camille gave a summary of progress to date. Sent paired regular and antistatic bags to 14 sites to obtain 26 pairs of samples and 25 paired travel blanks in the different bags. More work is needed with the data obtained. More work is needed to come up with criteria for making the switch to the antistatic bags. Camille suggested more deployments during the hot summer months. Does decrease breakage of glass jars and improves sample integrity during shipping. Feedback from operators is very positive.

I. Long-term Archive Update: Archive plan was sent for QAAG Information on 2/5. Greg and Melissa sent written comments. Archive plan has been put into place beginning 1/2019. Greg likes the plan except for using the CO00 site due to operation inconsistencies and lack of precipitation there. Richard and Camille will talk to Greg offline.

Routine Business

- A. Site Survey Status (EH, MJ) – Eric and Maria were not on the call. Eric was on a plane.
- B. Site Operations Update (RT) - Shutdown did cause some equipment failures that went unattended, but no USGS N-CON sites were problematic. Students at UW have developed a step-by-step SOP for ACM sensors and motor box testing and repair. Rolling out Androids to sites continues. Now sending out testing instruments for I-phone WIFI raingage communication.

Next Meeting: Possibly before spring meeting or later in the summer.

Leftover OLD Business

- A. Precipitation sensor study wrap up: Greg will look for the data, but this is probably now a moot point. The general consensus is that the superior sensors that were tested at the IL11 site by Mark Rhodes were the Theis Clima and new CAPMoN grid sensors. Greg volunteered to try to package the data into an online data release, but no promises.
- B. PTGE bottle evaluation wrap up: Bottle was approved by NADP in 2018 and is now in use by MDN. Dave Wunerlich indicated Ryan Nelson reported that M. Rhodes had all of the comparison data, and Greg might have that information now. Greg will look for the data. Perhaps these data could be summarized in a brief document on the web site. Dave W. indicated that Ryan thinks PETG bottles are reducing evaporative loss due to a better seal between thistle tube and PETG bottle mouth.
- C. MDN sample evaporation: No suggestions for action. This is still an open issue, but perhaps PETG bottles are helping to reduce evaporation.
- D. Methyl mercury sub-sampling methodology: Not discussed in detail. MeHg is subsampled from THg samples and composited based on sample volume. This creates a pseudo-precipitation-weighted MeHg composite sample. Improvement of the method has been a topic of discussion in the past. There are 9 MDN sites that have samples analyzed for MeHg. Mark Olson will reach out to those sites to determine their continued interest in the analyte. Greg indicated that he is one of the few people (only person?) to have evaluated the MeHg data set with observations presented at Canada AGU in 2015. There are >80% non-detects and most of the samples with MeHg had observable debris in them, indicating the possibility that MeHg is being made in the samples after collection, but that is not confirmed by any data. Greg questioned whether MeHg is an official analyte and whether it is worth keeping. Bob said MeHg is on the web site.

- E. Belfort gage 6-inch crossover point evaluation: Greg indicated that it would be better to just get e-gages installed at the remaining Belfort sites. There is an effort in the PO to try to procure more e-gages. Greg suggested once again that there should be an effort to round up instruments from inactive sites as he has done by acquiring the NM98 Noah-IV. There is an OTT Pluvio-N (older model) at a site in IL (IL78?) that we can have.
- F. Debris in MDN samples: Site operators report no debris in their samples, and by the time the samples get to the HAL, they have visible debris in them. Might be precipitating organic carbon. Dave W. indicated that sSamples with debris are not necessarily invalidated. HAL believes that its observations of debris are accurate.
- G. Reconciliation of precipitation depth for colocated NTN and MDN sites: At these site, the NTN and MDN collector depths are obtained, and they are different. Which one should we use for substitute precipitation (sub_ppt)? Bob Larson indicated that resolution of this should be easier once the HAL moves to WSLH. Bob suggested that the logical thing to do is to simply take the larger of the two sample depths as sub_ppt.

Meeting adjourned at approximately 3:00 p.m. Central.

Respectfully submitted,

Greg Wetherbee, USGS
QAAG Secretary

March 2019 Minutes Approved 6/24/2020 Via Online Survey Monkey Vote – 100% approval