

**NADP QAAG Minutes**  
**Wednesday, October 11, 2023**  
**1:00 PM – 3:00 PM Central**

Join via MS Teams

Attendance: Greg Beachly, Katie Blaydes, Christa Dahman, Noel Deyette, Dana Grabowski, Eric Hebert, Mark Kuether, Winston Luke, Amy Mager, Nichole Miller, Zac Najacht, Melissa Puchalski, Martin Shafer, Tim Sharac, Marcus Stewart, Cheryl Sue, Richard Tanabe, Greg Wetherbee, Jason Worden

**1. Site Support Issues/Questions – *EEMS (Eric Hebert)/PO***

- a. Update on EEMS Site Audits – **Eric:** on track to be completed as scheduled.
- b. AMNet Audits – **Jason:** Went to NJ30 and NJ54 with Vid Grande and learned about the AMNet auditing and did some maintenance on the equipment. Vid also went to two sites in New York (NY98 and NY20). Vid is reviewing all 2022 data and has one site left to do, so 2022 data should be done by Friday (10/13/2023).
- c. Lingering (reoccurring) field Issues? I.e. windscreens, pesticides... - **Eric:** trying to get the database tables straightened out due to a lot of issues with GOES transmission from the USGS sties. Revisiting the SOP for bag sampling for NTN sites. It is noted that there could be the introduction of potential contamination and bias on the volume measurements with the way site operators are performing the bag change out. Currently, in most cases the site operator is weighing the bucket with the bag in it with no lid. Then they are putting a clean lid on it, going to the site, and then moving that lid to the sample being collected. There is then long exposure of either the sample being collected or the clean bucket/bag being installed. Suggestion is put the lid on the bucket before weighing and keep the same lid with the same bucket/bag for the whole time. So when they get to the site they will have a bucket/bag that is sealed and have the lid from the previous week to put on the sample being collected. This will also reduce the bias of volume measurement since right now they are just writing down the pre-measured lid weight and there is variation amongst scales.

**Amy:** It is thought that what is being suggested is the current procedure, but it can be a confusing process and we will look into how the SOP is written and make the necessary edits/changes.

**Eric:** It may be best to remove the lid weight on the FORF and have just a total weight without precipitation (bucket, bag, and lid).

**Nichole:** Confirm the SOP and all training is clear for site operators. Possibly change the FORF when reordering?

**POST MEETING:** I did read the SOP and it is stated that the same lid should be brought back to the site for collection and the new bucket/bag should have its own lid. There could still be a volume bias based on not weighing the lid, so we can revisit the FORF/SOP about doing a bulk supply weight (bucket, bag, and lid).

**2. Site Operations – *Richard***

- a. Overall Update – **Richard:** Reiterating the fact that the GOES sites have had consistent issues. Updating transmitters from the 325's to 321's – whole program rewrite and getting help from

EEMS. Biggest equipment issue is the block sensors on the ETI NOAH IV rain gauges (currently 36ish). Did get a loaner/tester from ETI – Eric took it out in the field to a few sites.

**Eric:** Hopefully have fixed 3 of the 36 sites with this issue. Had to use the jumpers off of the tester to fix the issues at MN97, so the tester is currently inoperable.

**Dana:** Added an external trouble ticket system where external agencies can submit issues they would like EEMS to work on that aren't necessarily on their list of sites to visit – it has been useful.

### 3. Wind Rose Plot Survey Participation – *Tim*

**Tim:** (sharing the results from the wind rose plot survey) Most sites have an obvious consensus – there are a just a few with split votes. What is the next step? Should we draft a letter to let the site operators/sponsors know if they are interested in reorienting their collector we have supporting data?

**Amy:** Agree that we should draft a letter and may be worth putting something in the SOP.

**Tim:** Thoughts on the few that don't have a unanimous consensus?

**Eric:** Is there a way to look at volume weighted precipitation events?

**Dana:** Also precipitation type would probably be useful. If it's snow that is usually when there are issues with blowing and collectors not catching a lot of it.

**Tim:** It may start to get difficult for the website to generate that type of data, but will look into it. May have a follow up meeting on hammering out the split decision sites and the draft letter.

### 4. External QA Update – *Noel*

**Noel:** For the inter laboratory comparison program, there are still 11 labs involved for NTN and 9 labs for MDN. Currently, there will be 8 MDN for the next quarter since ERTC in Thailand is having some reapplication problems they need to figure out. Shipping costs are extremely high, especially for Canada. So USGS is open to options if there are other domestic labs that anyone knows that may be interested in participating in the program because we don't know if it is sustainable to really keep doing all of these international shipments long term. Publication updates – data is released for the 2021-2022 external QA and that is available online; the 2021-2022 SIR report is in review and anticipating publication in spring 2024.

### 5. System Blank and Field Audit – *Amy/Zac/Noel*

a. Current operations – **Noel:** All of the field audit samples have now been shipped out and system blanks. Have been receiving a lot of surveys back and reading the comments section. There seems to be some confusion on instructions for both programs (FA and SB) so we may want to revisit that. USGS is working on updating their SOPs for both inter lab and field audit processes and those will be sent to the NAL for review.

b. Future plans? – **Amy:** NAL is still shipping system blanks and that has worked out well. The efficiencies and potential cost savings just weren't there for the field audit samples so USGS will continue to do those.

**Noel:** The FA samples were a lot of work initially, but now that the details are worked out next year should run smoother. The cost of the solutions to make these high purity samples are increasing so looking into using the SRS USGS solutions in the future. We will run tests of those solutions through the NAL before shipment to make sure there are the levels were are intending. We may want to reconsider the scale of this program? Currently shipping to about 100 sites per year with a general return rate of about 60%. Also, note that some operators are

noting that they are shipping in this sample on the same day they write down that it is deployed and it should be sitting for 24 hours so we may need to flag these samples if possible for not following protocol.

6. **Sampler Colocation Update – Noel**

**Noel:** Both are operating well and we are receiving data. They are anticipated to run through 6/1/2024. Due to budget it is still up in the air about future collocated sites.

7. **Lab Investigation Projects (current and upcoming)**

- a. Hg Passive Samplers (*Martin/Christa*) – **Christa:** Have done field comparison with Winston’s help against the Tekran and then the passives at Eagle Heights. Concerns with a low bias of the passives samplers compared to the Tekran. Want to do an inter comparison with ECCC and maybe Tekran. David Gay was going to look into coordinating that.  
**Martin:** What we are seeing is concentrations that are basically ambient mercury concentrations and the Tekran measurements are consistent with what the community believes is closer to reality. There are three Tekrans and then duplicate passives samplers in the study and we were getting 55-60% recovery on the passives compared to the Tekrans and the three Tekrans had an overall standard deviation of measurements of about 4%. We need to understand why we are seeing a much lower level in the passives.  
**Winston:** Have the Q1 numbers (January-March) from Katrina McSween and the ECCC passives data is substantially higher than the Tekran numbers – about 25% higher.  
**Christa:** Our reference material QC is coming out really well. Had discussed what a typical blank is because we have seen the blanks kind of creeping up, but expected for longer deployments. Katrina supplied blanked data that had a pretty wide range. If there are going to be random high blanks we may need to increase the deployment time to more than a month to get around that uncertainty. Discussion in MELD at the fall meeting.
- b. PET vs. PETG Study (*Christa*) – **Christa:** Redid the PET vs. PETG bottle study from 2018 to confirm PET is an appropriate material to use for MDN. Study Conditions: 60 total samples; 7 blanks for each plastic, 7 spikes for each plastic, 5 natural (NTN) samples in duplicate for each plastic, 2 additional natural sample replicates prepared directly in analysis vial for “true value” estimation. Bottles held with standard pre charge of 1% HCl for 1 week before use. Samples stored in bottles for 1 week before BrCl oxidation for analysis. Samples then reanalyzed at 4 weeks. Performance criteria was established, most based on procedures and methods that we already have in place. Blanks must meet our lot lab testing criteria (mean concentration below our MDL and no individual result above our LOQ). Wanted spikes to have +/- 15% recovery (6.8-9.2 ng/L). Wanted less than 25% RPD for the natural sample matrix duplicates and the RSD for all results of the sample to be less than 15%. And wanted the spike free samples to have an RPD of less than 25%. The biggest issue noticed was the increase in blank concentration over the 4 week period – all of the PETG blanks failed criteria at the 4 week mark. One of the PETG spikes failed high at the 4 week mark. One of the PETG spikes failed low at the 1 week mark, then passed at the 4 week mark. Quite a bit of variability in the natural samples especially in the vials (could be loss through the septum in the VOC vials). In general, pretty good agreement among duplicates. Also processed data with a blank correction. Ran t-tests on sample types (results below).

Sample Type	t-test Comparison	p Value	Outcome
spiked	Initial PET vs. Initial PETG	0.138	accept null hypothesis; results are the same
spiked	Final PET vs. Final PETG	0.475	accept null hypothesis; results are the same
spiked	Initial PET vs. Final PET	0.000	reject null hypothesis; statistically significant difference
spiked	Initial PETG vs. Final PETG	0.001	reject null hypothesis; statistically significant difference
spiked	Initial All vs. Final All	0.000	reject null hypothesis; statistically significant difference
blank	Initial PET vs. Initial PETG	0.998	accept null hypothesis; results are the same
blank	Final PET vs. Final PETG	0.022	reject null hypothesis; statistically significant difference
blank	Initial PET vs. Final PET	0.004	reject null hypothesis; statistically significant difference
blank	Initial PETG vs. Final PETG	0.005	reject null hypothesis; statistically significant difference
blank	Initial All vs. Final All	0.003	reject null hypothesis; statistically significant difference
Natural-1	Initial PET vs. Initial PETG	0.033	n too low; do not evaluate
Natural-1	Final PET vs. Final PETG	0.054	n too low; do not evaluate
Natural-1	Initial PET vs. Final PET	0.170	n too low; do not evaluate
Natural-1	Initial PETG vs. Final PETG	0.124	n too low; do not evaluate
Natural-1	Initial All vs. Final All	0.006	n too low; do not evaluate

**Blank Corrected**

Sample Type	t-test Comparison	p Value	Outcome
spiked	Initial PET vs. Initial PETG	0.138	accept null hypothesis; results are the same
spiked	Final PET vs. Final PETG	0.527	accept null hypothesis; results are the same
spiked	Initial PET vs. Final PET	0.048	reject null hypothesis; statistically significant difference
spiked	Initial PETG vs. Final PETG	0.124	accept null hypothesis; results are the same
spiked	Initial All vs. Final All	0.947	accept null hypothesis; results are the same

In conclusion, most of our predefined criteria were met and the failures that we saw were predominantly associated with the increasing blanks in both material types, but the PETG is the only one that truly failed. The PET provided noticeably better stability and precision and should be accepted as a useable material for MDN. There will be another presentation on this in NOS. Could propose a motion of acceptance then.

- c. TN/TP (*Katie*) – **Katie:** Not much analytical progress on the research. We still need to look into the pH issue. We have currently stopped sampling at the Arboretum in Madison and John Walker’s site in Duke Forest, due to not having the time/staff to run the samples. There has been a recent push for these measurements by the Park Service so we are putting them back on the forefront of our list. So the hope is by the next fall meeting, if all goes well with time and manpower, we should have some updates with results.
- d. AMoN Alpha Samplers (*Katie*) – **Katie:** We are looking into the cost savings aspect of switching from the Radiello samplers (Italy) to the Alpha samplers (UK) for AMoN. The materials and shipping costs would be reduced and the prep time would be reduced. Looking at about a 30% savings overall. There is already literature in place stating that the Alphas are comparable to the Radiellos. Abby and Katie have been working hard at figuring out the method and prepping the samplers and cores for the Alphas. Have had conversations with the UK lab to figure out method issues here. Currently have a collocated study set up here at the lab. As of right now, we are seeing a low bias on our measurements and pretty sure it is the analytical method. There will be a poster at the fall meeting with more information.  
**Melissa:** Concerns about how the site operators will handle them in the field compared to the Radiellos.
- e. MDN Bag Testing (*See NOS update*)
- f. Automation (*See NOS update*)

8. **Lab QA Issues Update** – *Nichole*

- a. ICP backup – **Nichole:** We had another issue with the ICP being down for a longer period of time so it brought up the idea of a backup instrument again. Still investigating getting our method set up on the other ICPs in the lab (Perkin Elmer). It is definitely feasible, but we just need the time with our staff and the Metals staff to work on their instrument and figure out the software and run some tests.
- b. Future of our FIA instrument – **Nichole:** The current FIA instrument (Hach LACHAT) has been discontinued and they will stop being serviced in 2025, so we have started looking into a new instrument. We explored a few, but have really focused on the FIALab instrument.  
**Katie:** The soils group has already purchased and is using it. This is considered a larger purchase so it must be approved and we are on the list to make this large purchase hopefully next fiscal year.  
**Cheryl:** ECCC just purchased them and shared some data with Katie. Will send the final reports once they are processed.

9. **PFAS QA** – *Martin*

- a. Bag Testing – **Martin:** All of the bag testing was very promising. There was just a small loss of some of the sulfonamides. The field and lab blanks were great, even better than the buckets themselves.
- b. Network Field QA – **Martin:** Information focused on the EPA sites which there are 11 at this point. We have collected field blanks, field spikes, and trip blanks on a quarterly basis from all of these sites. We have data for some of those sites for three years or so. Well over 200 field QA samples have been summarized, submitted, and processed and the data synthesis is in process. Expected summary by the fall meeting. It will all be a standalone document but pieces will go into at least two of the papers that are currently in production. We have also synthesized all of the triplicate collocated data from Duke Forest. That will be part of a manuscript that is describing the first year and a half of the PFAS program. There was also a year of duplicate collecting at Devil's Lake. So overall, this will be a large QA data set that will be available in multiple manuscripts and publications.  
**Melissa:** We have had several years of data go through the QA audits successfully. Currently working on the 2022 data.  
**Martin:** Melissa has spearheaded the effort of the 12 point plan over the last 6-8 months to begin the process of making the PFAS collection a formal subnetwork. It has been circulating for comments and a summary of the document will be presented at the fall meeting. One other quick note, of all of the nearly 1000 samples collected over the last three years the first year and a half of that have completely gone through the external data audit and effectively have been released for public review and manuscript production. All of the 2023 data through May have also been submitted to EPA.

10. **Data Review** – *Zac/Dana/Mark*

**Zac:** Making the effort to get 2022 data finalized to get in Mark's hands for final checks and to make the maps. We had two interns from APHL over the summer that helped quite a bit with data review. Looking at being through March 2023 data by the fall meeting. Have had meetings on how to implement the branched approach to accomplish review quicker and seeing who is

able to help out with these tasks. In the process of getting an APHL fellow for next year to help with data review.

**Mark:** David noted some high values on the charts provided and Zac and Mark went through and confirmed them. Overall, been bouncing charts and data off of David and Zac when issues arise. Been working on incorporating these issues and resolutions into the SOPs in progress so we can catch them and fix them earlier.

**Zac:** Working on how can we cut down the amount of time Mark needs to spend on processing i.e. is there something we can catch in preliminary review or automate. Just looking to streamline that process so we can get data to the web quicker and more consistently.

#### 11. QA Documents – *Nichole*

- a. NADP Lab QAR 2022 – **Nichole:** The 2022 QAR is undergoing internal reviews currently. Hopefully have that to QAAG for external reviews in the next month or so.
- b. NADP Lab QAR 2021 on website – **Nichole:** There are minor updates (grammatical edits and figure/table descriptions) to be done and then will get a copy on the web.

#### 12. Audits – *Nichole*

- a. Internal Audit (System and Method) – **Nichole:** Unfortunately missed the internal audit last year with Camille leaving and Nichole taking over at the end of the year. Currently working on doing an internal systems and method audit for the NAL. The systems audit is complete, just working on writing it up and getting it out to supervisors. No major issues observed that need to be discussed. The only overarching ‘issue’ noticed was the need to implement more cross training on tasks and instrument platforms. Will start working on the method audit next.
- b. External Audit – **Nichole:** We will have a combined PO/NAL external audit in 2025.

#### 13. PT Updates – *Nichole*

**Nichole:** There will be a detailed visual PT update at the fall meeting. Quick update for now. We completed the spring ECCC PT samples for NTN and MDN. Overall really good results. A slight positive bias for our cations on the ICP, but still within 110% recovery. Fall set of ECCC PTs will be ordered soon. We have completed both the spring and fall set of USGS SRS PT samples. These are a snowmelt matrix and can have a bit higher concentrations. We had a low recovery for Cl, but the MPV was 8.49 which is pretty high for what we test. But no general bias across the board. We have run the spring WMO samples (fall will be ordered soon). Again, a slight positive bias on the cations for the ICP but still within 110% recovery. This could be an issue to look into. I did pull the analytical runs for these on the ICP and there was no concern with the calibration or the in-run QC results. Lastly, we participate in the USGS inter lab comparison PT samples (NTN and MDN) and just pass the full data set onto Noel at the end of the year.

#### 14. MDN bottle contamination – *Amy/Nichole/Dana/David*

- a. ‘Final’ updates – **Dana:** Mostly done with reviewing the data that would contain the contaminated bottles. So for the 2022 data set, there were 473 wet samples and 136 were invalidated (29%). There were 30 DF/DK samples and 14 were invalidated (47%). And there were 114 dry samples. These are the numbers we were expecting.  
**Mark:** Made some adjustments to the mapping criteria. What we did for the sites that had invalid samples, one of the mapping criteria involves the period of valid samples over the total charting period and so to adjust it we reduced the charting period by the length of those invalid samples. So we didn’t count that against them.