

**Minutes of the 2015 Spring Business Meeting
for the
National Atmospheric Deposition Program
Network Operations Subcommittee
Asilomar Conference Center, Ocean Grove, California
Tuesday, April 14, 2015 – Wednesday, April 15, 2015**

Officers: NOS Chair: Amy S. Ludtke, U.S. Geological Survey (USGS)
Vice Chair: Richard H. Tanabe, Environment Canada
Secretary: Gregory A. Wetherbee, USGS

Tuesday, April 14, 2015

The meeting was called to order by Amy Ludtke at 1:30 p.m.

1. **Approval of Fall 2014 Joint minutes (Indianapolis, IN) – Amy Ludtke (USGS)**

Motion to accept: Melissa Puchalski, USEPA

2nd: Jason Karlstrom, Eurofins, FGS

Motion accepted unanimously.

2. **1:32 AMoN Status – Melissa Puchalski (USEPA)**

- a. Network is growing with 92 sites, including states of AK and WY
- b. Travel blanks look good. TB conc. = 10th percentile of all AMoN data.
- c. 2013, seasonal patterns evident
- d. 2015, blanks look cleaner due to discovery that kimwipes might be contaminating travel blanks.
- e. 2014 precision <15% error.
- f. 66 sites are co-located with CASTNET sites.
- g. One can now look at NH₃ contribution to total Nitrogen at CASTNET sites.
- h. NH₃ not decreasing anywhere.
- i. Site Characteristics Pilot Study: 3 sites with soil, vegetation characterization associated with fluxes at AMoN sites.
- j. Spatial Variability Study – Will benefit TDEP Hybrid Maps. Look at distance where variability stabilizes.
 - i. How far out can we interpolate concentrations?
 - ii. Evaluate gradients in NH₃ from east to west.
- k. Coweeta Flux Study (SANDS) and MARGA Study are ongoing.
 - i. Beltsville nitrogen train – looking at different N pollutants (MD99) and diurnal patterns. Prelim results look good. MARGA running there too with good comparison between NH₄⁺ and NH₃.
- j. There are 5 new articles using AMoN data.
- k. Gary Lear asked about 0.2 mg/L NH₃ trip blank (TB) level, and he emphasized why that level is important to the quality of NH₃ data. Either 0.2 mg/L NH₃ should be used to code data as "B" or used as an adjustment to data. Gary also pointed out that first 2 years of network, TB concentrations were much lower than the past several years.

- i. Chris Lehmann indicated that a lag time between TB and sample analyses makes application of the TB data to individual samples difficult. Tom Bergerhouse stated it would be arbitrary to flag certain samples.
- m. Gary Lear indicated a need to flag samples when $>[RL]$ and $<[TB]$. There is a need to understand TB data better.
- n. Gary motioned that CAL come to the next meeting with a report on AMoN travel blanks and their effect on the reporting limits.

Moved: G. Lear (USEPA)

2nd: Mark Rhodes (NADP PO)

Nay: Greg Wetherbee (USGS)

Motion Passed.

3. **2:00 p.m. USGS External Quality Assurance Report 2014** – Greg Wetherbee (USGS)

- a. NTN Interlab:
 - i. CAL's high performance is consistent with previous years.
 - ii. CAL data show negative bias within statistical control limits observed for NO_3^- and SO_4^{2-} .
 - iii. CAL's blanks are clean.
 - iv. Several labs had incomplete sample loads from shipping problems in 2014.
 - v. RTI Corporation joined program February 2015. Shipping to 9 Labs now.
- b. NTN Field Audit:
 - i. Three-year moving Network Maximum Contamination Levels are generally consistent with historical values, but increases are observed for Ca^{2+} , Mg^{2+} , NO_3^- , SO_4^{2-} over past four years.
 - ii. Maximum NO_3^- and NH_4^+ losses continue to be much lower than recent past.
 - iii. E. Hebert asked if there is a difference between ACM and NCON for FA and System Blank? Greg indicated that he did not know, but that is a good question for the upcoming QA report.
- c. MDN Interlab:
 - i. HAL demonstrated continued high performance consistent with previous years.
 - ii. One sample out of statistical control.
 - iii. Slight positive bias (~1 ng/L) July-Dec. compared to median from 10 laboratories.
 - iv. Timing of the shift in bias same as 2013.
- d. MDN System Blank:
 - i. Three-year Hg mass NMCL decreased from 0.54 to 0.34 nanograms Hg per sample.
 - ii. 2014 System blank samples show less Hg contamination than 2013.
- a. Co-located Sampler Program:
 - i. Last Water Year, sites at TN11 and KS32. This Water Year (2015), sites are at WA99 and ND11.
 - ii. At TN11, ETI median percent difference was 2.7%, and at KS32, OTT median percent difference was 2.6%.
 - iii. N-CON minus ACM median relative concentration differences (mg/L): Ca^{2+} (0.015), Mg^{2+} (0.001), Na^+ (0.002), K^+ (0.003), NH_4^+ (0.016), Cl^- (0.005), NO_3^- (0.049), SO_4^{2-} (0.041), Br^- (0.000), volume (20.8 mL); all positive.

4. **2:15 Site Survey Report** – Eric Hebert (EEMS)

- a. More shift from ACM to NCON collectors, no surprise
- b. More e-gages, many fewer Belforts
- c. Accuracy of Belforts as found still pretty good. As left after cleaning/adjusting is better. 6-inch turnover point is still a problem.
- d. Indicative sensor temperature test: Few sensors not quite above freezing but above ambient temperature. Rest of results look ok, and sensors are working when cold.
- e. Activated grid sensor temperatures are well within working range except for a few at 50°-60° C.
- f. E-gages don't require much maintenance interaction like Belfort. This allows bugs, mice, etc. to enter. Might want operators to enter gage periodically to chase out insects, rodents, etc. Batteries not checked either, allows deterioration. Periodic cleaning should be required.
- g. Power cords are not being maintained or protected.
- h. TX56 surge protectors is catching fire. This is the 3rd one!
- i. Corrosion problems still observed on pins where sensor wires connect on ETIs. Battery posts corroding on ETIs too.
- j. O-rings observed at one site provided by N-CON to stop leaking between funnel and chimney cap. Use of o-rings was never approved. HAL instructed to get rid of them for contamination issues.
- k. Missing chimney caps on MDN ACMs.
- l. Lid liner was installed upside down.
- m. Issues: fewer buckets held incorrectly, fewer fingers in buckets, but maintenance needs to be improved.
- n. EEMS is trying to reach out to operators with resources for help.
- o. Internal QA: 0.38% error on dual data entries.

5. **2:52 AMNet 2014 Status** – Mark Olson (NADP PO)

- a. AMNet sites up to 22, and all sites are currently active.
- b. Adding MI09, University of MI Biostation, Pellston (LADCO funding)
- c. Possible MI site near Detroit coming?
- d. CA48 needs funding to keep going.
- e. OK99 funded through 2015.
- f. Mark's 2014 field season included: 14 sites, 16 visits, 17 instruments, including AK03, AL19, FL96, GA40, ME97, MS12, NU15, NY20, OH20, OH52, TW01, UT97, VT99, WI07.
- g. Mark is trying to spend 1.5 days at a site (up from 1 day).
- h. 2015: 5 sites so far, 3 with major repairs, and 10 pending.
- i. All 2013 data are available except MD08 site.
- j. Half of 2014 data now available, with 100% validated, 6 sites in backlog, and waiting on 3 sites.
- k. Stopped co-located operation at WI07.
- l. Need to improve upload times and QA database upgrade.
- m. 2013 QA Report is done! Need to address certifications that are "out of tolerance." Mark has a new policy to test flow meters prior to each visit.
- n. 2014 QA Report is done except for last table (% completeness by species). Data validation needs to be complete, and then report will be complete.
- o. International Conference on Mercury as a Global Pollutant 2015: Mark has 2 posters, 1 oral presentation, and 1 training course.
- p. Continuing 2014 data validation. Going to Asia for outreach.

- q. Mark Rhodes added: Let's do a training Webinar! M. Olson: This summer!
- r. Rhodes: State of IL has 2 Tekrans in disrepair. Any interest in getting them up and running with LADCO support? Olson: Let's talk to Donna at LADCO.

3:00 *Break*

6. **2:45 Mercury Litterfall Status** – Marty Risch (USGS)

- a. This is the Litterfall Initiative's 5th year of operation.
- b. Cost for participants is a \$2600/year add-on for MDN.
- c. Litterfall = ng Hg/g litterfall x litterfall catch (g/area) = Hg mass/area
- d. Network has 29 MDN sites in 16 eastern US states with annual litterfall, with data available 2007-2013.
- e. As of autumn 2014, network had 13 sites, with data pending, plus PR20 monthly monitoring.
- f. Average total Hg deposition (wet + dry) was 53% of dry deposition as litterfall deposition
- g. PR20 El Verde Site preliminary data presented for 10 of 12 months. Deposition is higher than the continental U.S. maximum, but percentage of total Hg deposition is similar to continental average 2007-13.
- h. Future: more participants, archive from 5 years freeze dried and available, USGS Hg Lab completed analysis of Hg isotopes in 32 archived samples at 12 MDN sites from 2007-09.
- i. Draft Journal article on litterfall Hg, 2007-13 in progress.
- j. Mark Rhodes: How does archive analysis compare to initial total Hg values? Marty: It's an interesting comparison, but might be totally different. More work to be done to get at this.
- k. Kristi Morris (NPS): Monthly collections in west (NPs) are possible. Stay tuned.
- l. Eric Prestbo (Tekran) took podium with a proposal for litterfall network:
 - i. Hypothesis $\text{Sum}(\text{leaves}) < \text{what is in collector as litter decomposes and is washed, whereby Hg is leached into the ground. Elemental Hg in soil might also be incorporated into leaves on the bottom.}$
 - ii. Sub-sample leaves into clean containers as falling on rain-free day over a few hours.
 - iii. Use multiple collectors to improve representativeness.
 - iv. Sub-sample 3 or 4 times over period of standard sample.
 - v. Measure mean Hg concentration and dry mass in each subsample.
 - vi. Compare sub-sample values with bulk sample values.
 - vii. Call this "litterfall deposition" not "litterfall dry deposition".
 - viii. Need to calculate number of samples required to be able to have desired level of confidence in results.
 - ix. Leiming Zhang (Environment Canada) agreed that it was not "dry deposition", and he generally endorsed experiment.
 - x. Marty agreed to do experiment in 2015, and perhaps USGS Hg Lab could provide analytical work.

7. **3:15 Equipment Testing** – Mark Rhodes (NADP PO)

- a. Precipitation Sensor Study
 - i. The study includes 18 sensors at IL11.
 - ii. Sensors include ACM 7 and 11 grid, Thies optical –versions, ETI new and old, Eigenbrodt, traditional CAPMoN, new CAPMoN, and Thies rain monitor (grid).

- iii. Data for open/close status duration and lid cycles is collected.
- iv. Similar behavior is observed between Thies sensors with N-CON settings and standard factory settings, and the Thies rain monitor too. Other manufacturers had greater variability.
- v. There is less consistency among other (not Thies) manufacturers.
- vi. Marty Risch and Kristi Morris: What is the conclusion? Mark Rhodes: Prefers Thies behavior due to consistent performance, whereas more variability among grid sensors. Mark is also encouraged to see results for DC version of the new CAPMoN sensor. The CAPMoN sensors seem more robust and versatile.
- vii. Mark fielded many questions about sensors. Generally, the study will go another year to test the CAPMoN sensor more thoroughly, but a scenario whereby a Thies sensor configuration and possibly the CAPMoN sensor could be the replacements over the long haul. Tom Bergerhouse mentioned that consistency is not the same as accuracy – is it opening when it should? Mark Rhodes: For the most part, yes, the Thies and CAPMoN sensors appear to open consistent with rain-gage measured precipitation.
- b. Electronic Belfort Rain Gage:
 - i. No data filtering occurs with Belfort. No algorithm was provided by Belfort, and algorithms tested performed poorly.
 - ii. Even with dual Alter shield (MD99), data was bad, even worse.
 - iii. Performance was not impressive.
 - iv. Recommended Action Items: 6 months more data
 - 1. Use Geonor Algorithm to filter data to see if this improves performance.
 - 2. Collect 2 full years data
 - 3. Prepare a white paper, to document testing and conclusions

NOS meeting broke for the day at 4:27 p.m.

Wednesday April 15th

- 8. **8:08 a.m. SCUAM Pilot Urban Network** – Richard Pouyat (USFS)
 - a. Pam Templer (Boston University) and Tom Whitlow (Cornell Univ.) gave the presentation over the phone.
 - b. Creating a sub-network of monitoring stations for urban centers to characterize deposition hotspots.
 - c. 50% of population lives in urban centers, projected 70% by 2050.
 - d. Urban centers are hotspots for deposition
 - e. Sites with >400 people/km² within 15 km radius were evaluated
 - f. Examples of current urban sites are NY06 in Bronx, NY, and OH27 rooftop collector.
 - g. Brooklyn Grange Rooftop Farm is testing bulk and resin collectors.
 - h. Particle counters on the roof and 3rd floor of building collecting data.
 - i. PM-2.5 data suggest traffic is source of particulates.
 - j. Boston – measured urbanization and collected resin collectors for Nitrogen (N).
 - k. Boston – along urbanization gradient, N increased from rural to urban.
 - l. Boston – increase is only significant for NH₄⁺ and total N.
 - m. Compared empirical to model results, and model values overestimate NH₄⁺ and underestimate NO₃ for NADP sites.
 - n. Need more complete estimates of regional loads to compare with trends for rural areas.

- o. Urban siting is difficult and needs to be done in coordination with NADP criteria.
- p. After Pam's presentation, Rich led a brief discussion on creating a sub-network.
- q. David Gay and Mark Rhodes mentioned siting criteria issues are important.
- r. There is a potential for analysis of solids from TO monitor filters.
- s. Mark Rhodes indicated that QAAG is supportive of SCUAM and that urban sites are already in the network. Chris Lehmann indicated that no new network is really needed unless there are new analytes. So, an urban network would/could just be operated within NTN.
- t. Mark Nilles offered to put Pam in touch with western researchers who make measurements in extreme environments. The roadmap for establishing new networks is well documented.
- u. Metals are desired for the urban network. That requires a 12-pt plan, which Frontier (Bob Brunette) has been working on but needs advocates. David Gay briefly described the 12-pt. plan process which is documented under Guidelines for New Initiatives.
- v. The presentation was well-received by NOS and the outlook for an Urban Network is promising.

9. **8:45 Proposed USGS Air Monitoring for Hg Isotopes – Marty Risch (USGS) & David Gay (NADP PO)**

- a. NADP Fall 2014 meeting presentation by Dave Krabbenhoft, and Executive Committee instructed PO to work with USGS on details for this study.
- b. USGS Hg lab (WI) to provide air sampler for selected AMNet and MDN site operators.
- c. USGS to provide equipment.
- d. Data about Hg isotopes in air are current a data gap. Isotopes can indicate sources of Hg in air.
- e. NADP PO to provide a letter of invitation to selected 22 AMNet and 4 MDN sites to participate in the study.
- f. The PO will distribute USGS-written SOPs to operators for the study.
- g. Chuck Sam (USFS) cautioned that carbon traps can collect other metals besides Hg.
- h. Traps will be removed weekly. Mark Olson is not sure that AMNet operators can accommodate weekly swap out, but some/most operators will likely be on board.
- i. Suggestions were given by Mark Olson and John Jansen (Southern Company) for Marty's letter to request participation among operators for the study.

10. **9:00 Bucket and bottle changing monitors -- Eric Hebert**

- a. Operators use a variety of different methods for bucket-on and bucket-off times, which makes a difference for buckets switched out, especially during events.
- b. Eric produced a sample-change monitor using a beam sensor where IR beam is blocked with bucket in place and not blocked when removed. Emitters run on 7V and detector 12V. Voltage regulator and switch closure installed to be compatible with collector voltage. Switch was tested at MD99.
- c. Eric wired sensor into datalogger on gage, and Bob programmed website to have field for bottle change. Voltage spike from beam detection has a time stamp for bucket change time.
- d. The system worked better for MDN than NTN due to shorter path for MDN versus angled path through bucket holder on ACM. Installation would be more challenging for an N-CON and may require a bracket to be made.
- e. Richard Tanabe is doing something similar at CAPMoN sites (See below).

11. **9:21 CAPMoN Network and Equipment Update** – Richard Tanabe (Environment Canada)

- a. MDN, 5 sites
- b. NTN CAN5 site in Freilighsburg
- c. SK12 hopefully running by end of summer. SK28 future is uncertain.
- d. NS01 is moving.
- e. Next generation of CAPMoN collector specifications:
 - i. Maintain bucket size
 - ii. Modular for shipping, easy troubleshooting and parts replacement
 - iii. Failsafe to prevent mechanical movement in event of lid mechanism restriction
 - iv. LED indicators for better viewing in sun.
 - v. Bucket switch data logging
 - vi. Other miscellaneous features were listed.
 - vii. N-CON designed collector using the CAPMoN bucket. N-CON used a pressure switch (button) for detection of the bucket's presence/absence.
 - viii. CAPMoN D400 is the next generation model.
 - ix. Linear actuator, new 3-grid pad sensor, no lid shield, 24V DC, Can run on solar (2 - 12V batteries with float charger) Data logging with bucket on/off.
- f. Flat Valley, SK site has 1 year sampling, 30 days missed.
- g. Running Eigenbrodt NSA sequential sampler
- h. Nancy Lance and Chul-un Ro retired.

9:50 *Break*

12. **10:15 Network Telemetry Options** – Bob Larson (NADP PO)

- a. Adhoc Committee: Bob, Mark Nilles, Kevin Mishoe
- b. Currently, NADP uses: 3 GOES satellite, 3 DSL, 3 cellular phone, and 3 radio telemetry installations.
- c. Satellite option: Use USGS/NOAA GOES satellite transmission
- d. Use USGS web interface, administered by Bubba Brossert in Arkansas.
- e. Use Campbell Scientific datalogger from OTT Pluvio II RMM or the ETI Noah-IV gages
- f. USGS interface can make preliminary data available for 90 days, then it's first in=first out.
- g. Up to 16 parameters can be transmitted in data string.
- h. Cost for GOES satellite is one-time equipment purchase of \$3,500, then free service.
- i. Digital Cellular option cost is one-time \$864 equipment and setup + \$8.50/month service charge.
- i. PO can absorb costs for cellular as billing can be frustrating.
- j. Bob put together 2 test kits with Raven Modems to test cellular connection at sites where cellular phone telemetry is being considered.

13. **10:30 Methyl Mercury Data pre-2002 Update** – Mark Rhodes (NADP PO)

- a. QAAG passed a motion to accept the data and serve it with other 2003-13 data, not as separate datasets. Explanatory notes for pre-2002 data will be included, and a field will be included to indicate which algorithm was used to calculate the concentration.

- b. Pre-2002 data had multiple files, formats, limited documentation, and no debris codes.
- c. No instrument values and no component volumes were included in dataset.
Therefore, cannot verify pre-2002 calculations or adjust them for pre-charge volumes.
- d. HAL's old procedure was to use a linear regression model to weight the top end of the calibration curve, but now a calibration factor model is used as the current algorithm, which matches EPA 1630 method.
- e. Mark showed an evaluation of the QA aspects of the data, including differences in seasonality between split and composite samples.
- f. Mark displayed maps showing spatial distribution of MeHg data. Both the graphs and maps visually indicate that there isn't a recognizable difference between the pre-2002 and post-2002 data. Therefore, the recommendation is to accept the pre-2002 data and serve all MeHg data as one dataset.
- g. Questions:
 - i. Should a calibration factor be applied to pre-2002 data? If so, HAL/PO would have to go back to the original calibration forms at HAL to get information, which is prohibitively time consuming.
 - ii. Should we continue to allow composite sampling based on differences observed?
 - iii. What is the effect of the cooling fan on MeHg concentration?
 - iv. What is the effect of the shelter heater on MeHg concentration?
 - v. What is the effect of component sample storage on composite MeHg concentrations?
- h. Eric Prestbo suggested that a checkbox form be used to make data users aware of changes in data quality before being allowed to download the data. Bob Larson indicated that this is doable.

14. 10:45 CAL's ICP Data Comparison Study – Katie Blaydes (NADP CAL)

- a. ICPOES used since Jan. 2004 using ASTM method
- b. Lab renovated to install new instrument
- c. New argon gas distribution system is coming, to be located outside the lab.
- d. New Agilent 5100 purchased and installed. Smaller than previous instrument, and reads in simultaneous dual mode.
- e. Other projects that want to look at more complex matrices or transition metals can be accommodated.
- f. Uses less warmup time, less argon gas, and less sample (3 mL).
- g. Percent recoveries are generally within 95-105 percent for all test solutions with Ca, Mg, Na, and K concentrations within the range of NADP-measured concentrations.
- h. Favorable results with approval by PO allowed use of new instrument to begin March 20, 2015.

15. 11:00 Leaky Bottles – Chris Lehmann (NADP CAL)

- a. CAL Looked at using 500 mL Nalgene single-use bottles for 1-time use to prevent leakage.
- b. A leak: <10 mL
- c. B leak: 10-100 mL
- d. C leak: >100 mL
- e. With deployment of "squishy bottles" in 2013, 74% of all bottles had no leakage. These were thought to be best solution to the leakage problem.
- f. Bottles are barcoded to track usage.

- g. Chris proposed a protocol whereby CAL will go through old stock of bottles and discard bottles after 6 uses as this appears to be the breaking point where bottles begin to leak more.
- h. In 2017, we could be down to bottles only used fewer than 6 times.
- i. Chris: Seek to put soft (a.k.a. squishy) bottles into system, while discarding bottles after 6 uses and phasing in newer bottles over time.
- j. Using 500 mL 1-time use Nalgene bottles could be a backup plan, but was not presented for approval.

16. **11:15 AMoN Travel Blanks** – Chris Lehmann (NADP CAL)

- a. CAL has sought better packaging to reduce breakage, and lower Trip Blank (TB) NH₃ concentrations.
- b. Current reasoning is that Kimwipes™ and Uline™ wipes are likely contaminating TBs.
- c. There are some ideas for shipping the samplers differently in glass containers to avoid breakage.
- d. More data are needed from further testing of the TBs that are now using filter paper in place of the laboratory wipes.
- e. Gary Lear (USEPA) suggested incorporating TB data into the reporting limit or develop a correction factor. Gary's concern is about contamination. While seasonality in TB NH₃ concentrations is common, the 2014 contamination level was higher in winter than normal.
- f. Greg Wetherbee (USGS) showed slides from Melissa Puchalski's presentation, indicating TB NH₃ concentrations are consistently at the 10th percentile of AMoN field data over the past several years, which should be considered excellent performance. Melissa's comparison of AMoN to denuder data also demonstrates that passive measurements are an excellent substitute for continuous denuder data.
- g. Gary countered that EPA is spending a substantial sum on samples, and cannot afford to have 80% invalidated. If CAL, which is doing all it can, cannot improve the process, then something will have to change about sample analysis. Perhaps CAL needs to investigate using the TB concentrations in calculation of the reporting limit. Discussion ensued on ways to investigate the issue.
- h. Greg Wetherbee recommended that Chris Lehmann talk to other laboratories with experience in using passive samplers for NH₃ and collect information on their TB performance for comparison.

Motion to adjourn: Richard Tanabe (Environment Canada)

2nd: Mark Rhodes (NADP PO)

Meeting Adjourned at: 11:31 a.m.

Respectfully submitted by:
Gregory A. Wetherbee, USGS
NOS Secretary