### Network Operations Subcommittee (NOS) Meeting Minutes 2016 NADP Spring Meeting April 26-27, 2016 Madison, WI

Officers: NOS Chair: Richard H. Tanabe (Environment and Climate Change Canada) Vice Chair: Gregory A. Wetherbee (USGS) Secretary: David W. Schmeltz (USEPA)

### April 26, 2016

Richard Tanabe called the meeting to order at 2:05 pm.

- 1. Approval of minutes from Fall 2015 (Rochester, NY) meeting Richard Tanabe Motion: Rhodes; second: Schmeltz; motion unanimously accepted
- 2. AMNet Update Mark Olson

AMNet holding steady with 23 operating sites; two new sites are being established - AL03 and IN21. The IN21 site is scheduled to begin on April 29, 2016. Two sites lost funding - VT99 and WI07. There is interest in establishing new sites in NJ (NJ05 and NJ30) and in Halifax.

In the last 12 months, 13 sites visited: AK03, AL19, FL96, GA40, MD08, MI09, MS12, NS01, 01NS, NS29, NY20, NY43, WI07; the instrument at only one site required repair. In addition, a visit was made to the APMMN water lab in Taipei, Taiwan. Upcoming site visits include: IN21, UT97, OH52, MI09 (all by the end of May).

Several changes to sites have been made: NY06 and NY43 went to GEM only as of January 2016; the site at Keji is moving to a new location; six sites have upgraded analyzers to the Tekran 2537X: AL03, AL10, FL96, GA40, NJ30, NJ54; some sites have increased inlet sampling temperature in response to some of Eric Edgerton's recent findings related to GOM capture and retention efficiency discussed at the Tekran Users Group meeting, September 2015 in Washington D.C. This change in sampling temperature is a deviation from the SOP.

Once the new shelter at the Bondville, IL site is in place, a new Tekran GEM monitor will be installed. In the future, speciation units would be added.

The CEEPAMS study has been running in Mark's "lab" (AKA, the barn). One of the speciation systems is being deployed at IN21, so Olson is looking for speciation components in order to continue the study.

Data availability – Most of the 2015 data are available (62%). Data and/or notes are needed for AL19, FL96, GA40, HI00, ME97, OK99, TW01. As reported in the Fall, password protected data are not actually "available." Although NADP voted to remove the password protection, the proposed action created discontent among a handful of AMNet site operations. Therefore, the password remained in place. Olson will propose an alternative compromise at the Exec meeting later in the week.

#### 3. AMoN Update – Melissa Puchalski

Ninety-seven AMoN sites currently operate; 68 sites are co-located with CASTNET to improve estimates of nitrogen deposition. AR09 and AR15 started in October 2015 (USDA ARS); Quapaw Tribe of OK began October 2015; ID07 CASTNET tribal site (Nez Perce) began December 2015; AK06 ended in October 2015.

The highest annual ammonia concentrations,  $18 \mu g/m3$ , reported at Logan, Utah. Annual concentrations did not vary much in the Midwest (IL/IN). The range in the Mountain region is  $0.5 - 3.2 \mu g/m3$ . (more variability between sites impacted by CAFOs – point sources). Seven year trends (2009-2015) for select sites (TX43, OK99, OH27, NY67, MI96) indicate a 7 -75% increase in ammonia concentrations. CO13 showed a 6% decrease over that same time period. AMON data featured in several peer-reviewed scientific journal articles, 2015-2016. Li et. al. (2016) showed shift from contribution to total N dominated by oxidized nitrogen to reduced nitrogen (1990-1992 versus 2010-2012).

Spatial Variability Study – Geostatistical analytical work to calculate a radius of influence for [NH<sub>3</sub>] that can be used for interpolating concentrations between AMoN sites. This is useful for the TDEP hybrid maps which were created by defining a radius of influence from CMAQ concentration grids using an inverse covariance model. The interpolation method was verified by actual measurements at: IL11, CO13, and NC25. The study suggests more AMoN sites are needed in emission source regions.

Flux Study – Creating a database of soil and vegetation chemistry and characteristics from 3 pilot sites (1 km radius)—Coweeta, Bondville, and Chirachaua. Information will drive a bi-directional flux box model. Goal is to provide flux estimates for each AMoN site; flux estimates will be offered and incorporated into the TDEP model.

Quality Assurance - With regard to QA, Melissa noted the QAAG motion that the Program Office (PO) or CAL will request AMON site operators to submit quarterly photos of the rain shields to the PO. EEMS visits most CASTNET sites annually and NADP wet deposition sites every 3-years. Sites collocated with EPA-sponsored CASTNET sites are checked and photographed every 6-months.

Quarterly travel blanks are used for limit of detection flagging. A note code of 't' is applied to ambient data less than the limit of detection for each quarter. Group discussion about what statistic to use to report network uncertainty

Melissa reintroduced a previously tabled motion to report AMoN uncertainty estimates in the database as median ( $\pm$ 2\*sigma) for the previous 3-years of triplicate concentrations for each quartile. For example, in 2016 AMoN uncertainty is calculated from the quartiles of all samples deployed during 2013-2015 time period. A motion to untable Melissa's motion was introduced and passed to facilitate further discussion. In the subsequent discussion, Chris Lehman expressed concern that the number of triplicates will vary. After the realization that there was not an alternative proposal, Melissa's motion passed.

There was some discussion about trends in travel blanks. Tom Butler's paper looked at this.

### 4. Equipment Testing - Mark Rhodes

AMoN Travel Blanks - Since moving away from U-Line Wipers and Kimwipes, the data are much improved. The median of all travel blanks is 0.09 mg/L

Sensor Studies - Continuing at Bondville

E-Belfort Raingage – Electronic Belfort Raingages have been running at IL11 and MD99. Mark reviewed three recommended action items from Spring 2015 NOS meeting:

- 1. Obtain 6 more months of data;
- 2. Use the Geonor algorithm (CRN) to filter data and see if it improves performance;
- 3. Prepare a white paper that documents testing and results.

All tasks were completed. A summary table highlighted results of the field study. The AEPG Belfort failed the field testing and usability criteria.

Field testing: Measurements from the AEPG differ from the official NADP raingage by more than 5%. A wetness sensor improved the performance of the raingage, but did not resolve differences completely.

Usability: Replacing a sensor requires changes to firmware settings and recalibration of the raingage. This would be beyond the skill of most site operators. There is no mechanism to incorporate event recorder (ER) or collector power measurements as part of the data stream.

Motion to accept the white paper report and end testing of the AEPG raingage: Wetherbee Second: Rogers Motion unanimously accepted.

Modified Thies Precipitation Sensor – Thies sensor has a big draw of power and runs hot. Wetness sensor from OR09 (USGS) being tested. Sensor triggers heater on Thies sensor to operate during precipitation. This is for use with N-CON collectors at DC power site. Testing at IL11 was performed with heater running as normal vs. power disabled. The sensor passed all the tests (target specs, controlled testing, field testing, and usability).

Recently, Thies has made major modifications to their PM. The heater and heater connection are different than the original PM. The operating voltage is 12-24V AC/DC; 4 heater modes (a always on, b when precip is detected, c external control, and d external on/off AND when precipitation is detected).

Rhodes noted four of these sensors have been ordered from Thies (cost \$270 each) for testing. One sensor will be provided in Mode A and the remaining three in Mode B. Both A and B modes will be tested. Rhodes expects there would be some power savings; but it's not clear how much.

Conley asked whether grid sensors could be used. Rhodes noted problems in the uniformity of grid sensor response.

Ludkte asked if there is a DC version of the N-CON in the works? Rhodes replied not that he's aware, though Environment Canada has proven that a dual powered (AC and DC) N-CON collector is do-able.

Lehmann asked if power consumption efficiency was due to an inefficient power inverter?

Tanabe teed up a motion to provide some direction on what to with the modified (OR09) Thies sensor?

Nilles noted that it's the Committee intent to have the same technology for the opening and closing of the lid, although sites can have different collectors based on monitoring objectives. A lower power

sensor would benefit solar sites; but now we are looking at three sensors -- the original Thies, the Thies modified (OR09), and the Thies new.

Rhodes suggested the new Thies may meet all our needs, and is also comfortable with the OR09 historical data.

Hebert suggested that collection efficiency should also be examined as well as completeness.

Motion to stop testing the modified Thies sensor and investigate collection efficiency after meeting completeness, and accept historic OR09 data: Hebert Second: Nilles Motion passes

One remaining issue is how to move forward on testing the new Thies sensors. Where and for how long? The discussion entailed providing guidance to Mark Rhodes on the field test. Want the least costly option to impact operations. Bergherhouse recommended having a data logger tied to the sensors to record responses. Nilles suggested a couple of questions to consider – Are the openings similar? Do we have a winner with NADP? Will it work with the Aerochem? Does it work or not?

Action Item for Mark Rhodes - Will the Thies work with the Aerochem? Are the opening and closing of the modified Thies the same? Mark should report out results of the test in the Fall.

N-CON Bucket Closure Switch Prototype -

Data logger constraints - Will it impact the CR1000 and the CR800? Bucket sizing constraints – Different heights and clearance with the N-CON collectors

Tanabe suggested it's not worth pursuing a study because of variable bucket sizes. Nilles moved to table the bucket switch discussion. Second: Ludtke Motion Passed

#### 5. Site Survey Report – Eric Hebert

In 2015, 118 site locations were visited and a total of 145 collectors assessed: 96 NTN collectors, 46 MDN collectors, 3 AIRMoN collectors, and 118 primary rain gages. Accuracy of Belforts as found was pretty good. As left after cleaning/adjusting is better.

As previously reported, 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. Power cords are not being maintained or protected.

Issues: holding buckets open by handles, fingers over bucket edges, no glove use for NTN and MDN; maintenance needs to be improved.

EEMS internal QA: .22% error on dual data entries.

New data logger initiative completed at approximately 20 sites- Upgrade Campbell data logger firmware; replace Bluetooth Dongle; reinstall or upgrade logger program; test Logger Link (for Android) and train site operator.

## April 27, 2016

## 6. USGS Mercury Isotope Study Update – Marty Risch

Potential exists for identifying isotope signatures linked to the origin and transport of mercury in environmental samples; a large scale dataset is needed as a reference.

USGS developed capability for production scale laboratory mercury isotope analysis.

USGS proposed air sampling for mercury isotope analysis at AMNet and select MDN sites (and non-NADP sites) – fall 2014; Exec Com approved

USGS developed and tested air sampler; constructed air samplers and mercury traps – 2015 Contacted potential participants at NADP sites – 2015 Standard operating procedure distributed – 2016 Schedule equipment distribution and sampling at participating sites – 2016

Air samples collected bimonthly every two weeks with a sampler mounted on a post, filter and soda lime assembly. Suggested that TGM was being captured in two gold traps for Hg isotope analysis. Prestbo indicated GEM is being captured not TGM. Two week sampling too long (Olson).

Samplers shipped to 25 sites (NADP & others) on April 1; first 2-week air sampling started April 5 and completed April 19; samples / traps shipped Another subset of sites to have samplers shipped in time for the next bimonthly sample Another progress report at the fall meeting.

### 7. Proposed Studies: AMoN Frequency and MDN Bottle – Mark Rhodes

AMoN - Special study to help develop DQOs and DQI's for AMoN by looking at weekly sampling and identifying how it may differ from 2 week sample concentrations. Weekly AMoN samplers deployed at 4 sites for 52 weeks. Weekly triplicates deployed for up to 10% of the deployment periods. Weekly travel blanks not shipped. Analysis performed by the CAL.

MDN Bottle - Explore the potential of replacing MDN bottles with single-use PETG Bottles. Single-use PETG bottles have a significantly lower background mercury concentration than do the washed/re-used glass bottles. This should eliminate the need to bottle blank correct the total Hg (and methyl mercury, probably) measurements. Sampling at three sites (IL11, WA18, and WI31) for 12 weeks. Weekly total Hg analysis of the 5 samples collected in PETG bottles for the 12 weeks. Methyl mercury analysis of the samples collected at IL11 and WA18 covered by Eurofins/FGS. Methyl mercury analysis for IL11 to use composite samples, as is currently done for the official MDN site at IL11. Methyl mercury analysis for WA18 to use split samples, as is currently done for the official MDN site at WA18. PETG bottles to be provided by Eurofins/FGS. Configuration includes: One dual-chimney N-CON collector with the official

(glass) MDN sample bottle and the PETG test bottle at each of the 3 sites; one modified ACM collector with the PETG test bottle at IL11 and WA18 <u>only</u>; current (glass) N-CON and ACM funnels and thistle tubes to be used throughout. Additional studies include redesign of the funnel and thistle tube to replace the current glass versions which are handmade, and susceptible to breakage.

# 8. USGS External QA Report – Greg Wetherbee

NTN Interlab - CAL continues to demonstrate high performance consistent with previous years; CAL 2015 data show a slight negative bias for  $NO_3^-$  and positive bias for  $SO_4^{2-}$ ; CAL 2015  $NH_4^+$  data are on target; CAL's blanks are clean. Note, several labs had incomplete sample loads from shipping problems in 2015. Sección de Contaminación Ambiental, Centro de Ciencias de la Atmósfera, Universidad Nacional Autónoma de México (UNAM) joined the program in Feb. 2016.

NTN Field Audit - Three-year moving NMCLs are increasing for  $NO_3^-$  and  $SO_4^{-2}$  over past 6 years; maximum H<sup>+</sup>,  $NO_3^-$ , and  $NH_4^+$  losses continue to be low.

MDN Interlab - HAL demonstrated continued high performance consistent with previous years; no samples out of statistical control; no bias compared to the median of values from 11 laboratories.

MDN System Blank - Three-year Hg mass NMCL decreased from 0.34 to 0.12 nanograms per sample. Important to note that participation in the system blank program is decreasing.

Co-located Sampler Program - Both sites had power failures causing missed samples and raingage data; SD08 / 08SD "went dark" for 6 weeks, resulting in missed samples for SD08, might not have data completeness to contribute to national maps.

# 9. Preliminary Data: Automated pH/Conductivity Instrument – Lee Green/Nina Gartman

Lee provided an update on the new automated pH/conductivity analyzer (EasyPREP TitrEC) the CAL received on 8/15. Instrument is made by SCP Science, Montreal, Canada. Purchased a cover for the TitrEC to ensure that the samples are not contaminated during the testing process which also keep the lab noise down. The instrument allows user to load samples and continue working on other projects. The resulting output is compatible with CAL's LIMS system which makes data upload easy.

Efforts to test the equipment are continuing. Testing different brands of probes, different changes of mV/S to allow longer stabilization time, and comparing 2, 3, and 4 point calibration curves in different ranges.

# 10. Update on NTN Bottle Leakage and AIRMON Bag Sampling – Chris Lehmann

- Bottles
- New bottles are better than the old
- As use bottles less, leakage is less
- Trying to limit bottle use to 10
- Some supply chain issues
- o Washers help
- AIRMoN Bags

- New AIRMON sample bags Single Seal; Single Seal + "Vertrod" Seal, "Vertrod" Seal
  + Single Seal
- $\circ$  \$.97 per bag
- Bag needs to conform to bucket specs
- Bag sampling at all AIRMoN sites started October 1, 2015
- Since October 2014, bag failure rate of ~1.5%; PA15 and NY67 no failures, all other AIRMON sites did.

#### 11. Effects of N-CON NTN Collector Bias on Temporal and Spatial Trends- Greg Wetherbee

- CA76/76CA
- Don't want to make changes that affect the trends. How do you tease out variability from collector versus signal from the environment?
- Collocated study sites
- N-CON minus ACM weekly, relative differences
  - N-CON collects a little higher volume of samples
- Has there been a trend shift?
  - Magnitude and application will tell you if it is significant
  - N-CON samples generally have higher concentrations
  - How important are small changes?
- Does new sampling have positive bias from a new sampler?
  - Will not make a big difference for big trends
  - Might make a difference for smaller trends/flat
  - Prestbo views it as change in detection limit
- Slope/trend detection limit
  - $\circ$  Trends ok
  - For critical loads might make a difference
- Is this a sensor issue (Rogers)?

### 12. Update on Tekran User Group Meeting – September 22-24, 2015 NOAA, College Park, MD – Mark Olson

Background -- The RAMIX study (2013) showed low bias for GOM; AL19 study (2014) good recoveries in zero air, low recoveries in ambient air; Independent research continued to show low GOM recoveries in ambient air (NOAA, SEARCH, NADP).

NOAA and NADP organized this meeting in College Park, MD to discuss results and assign future tasks.

More than 25 scientists from an array of academic and government institutions participated.

Challenges -GOM calibration sources; GOM very sticky; Need low concentrations (ng/m3); degrades to GEM, a species of interest

Use pyrolysis to reduce all forms to GEM - gaining confidence in this method

GOM MDL ~ 75 pg/m3

Several participants are performing experiments to look at GOM capture efficiency and retention. GOM is sticking to the inlet; Current sampling temp in the AMNet SOP is 50°C; if temperature is increased to

100°C higher concentrations are observed - NADP > 15%, NOAA 20%, SEARCH 50-100% increase in ambient concentrations; Olson and others are looking at changes in the SOP to increase temperatures (to 100°C) and potentially shorter sampling times.

## 13. Development of a National Pollen Monitoring Network – Chris Lehmann

At present, pollen monitoring is geographically and temporally limited and dependent on individual collectors, who are often unfunded and do not report data to a centralized network. Current monitoring and assessment efforts include: American Association of Allergy, Asthma and Immunology's National Allergy Bureau (NAB) pollen monitoring; Canadian pollen monitoring (Aerobiology Research Labs); National Phenology Network (NPN) Project Budburst; NOAA pollen dispersion modeling.

This effort to establish a new network is being coordinated through the Council of State and Territorial Epidemiologists (CSTE), with seed funding from the Center for Disease Control and Prevention (CDC). There are opportunities to potentially link to NADP. This could become an ad hoc science committee of NADP. The collaborators are considering adopting the NADP governance structure. This initiative has received seed funding from University of Maine to monitor NTN filters.

## 14. CAPMoN update – Richard Tanabe

Environment and Climate Change Canada Sites: 7 MDN (renewed Apr/16); 3 AMoN (renewed Nov/15); one NTN; 2 AMNet (renewed Nov/15); SK28 (MDN) started Feb 2016; SK27 (MDN) suspended Jan-Mar/16; restarted Apr 12<sup>th</sup>; site relocations of CAN5 (NTN) and NS01 (MDN)

Equipment update: Received 2<sup>nd</sup> prototype wet-only collector; minor tweaks from the previous version; additional software logging and control; load cell for bucket Migrating MDN operators to SC115 flash drives; ETI External Box

Additional solar array for prototype wet-only based on previous design in Saskatchewan -  $\sim$  1/3 the array size and battery storage

Started an inter-comparison at Egbert (ON07) site. The equipment includes:

- 2 MIC C300 wet-only collectors (CAPMoN precision)
- 2 prototype "D400" wet-only collectors
- 1 modified N-CON NTN collector
- 2 ETI gauges
- 2 EC standard rain gauges (stick)
- 1 Proposed Ott Pluvio 2

Showed testing to date Dec 15, 2015-Jan 11, 2016 (18 daily samples)

- Transition to weekly sampling at select sites
- Develop field transfer protocol for all samples greater than a volume to be determined during the inter-comparison to bottles
- Low volume samples would continue to ship in bags
- Initial daily-weekly inter-comparison sites
- Egbert Start June 1<sup>st</sup> combined with prototype

- Frelighsburg (CAN5), Penn State (PA15)
- Algoma, Lac Edouard, Snare Rapids, Jackson
- Second C300 and ETI gauge

Staffing updates -- Rosa Wu is CAPMoN Head; Cheryl Sue is CAPMoN Laboratory Supervisor

### 15. NOS governance and secretary selection process – Richard Tanabe

How do we select NOS officers? Topic came up at the Fall 2015 meeting. There is no salary or cash incentive; the benefits are fairly limited, but you get to work with some really great colleagues. As an action item, Richard will draft/circulate a NOS announcement that will encourage you to join the prestigious NOS management team.