

Network Operations Subcommittee (NOS) Meeting Minutes
2018 NADP Spring Meeting
April 10-11, 2018
Milwaukee, WI

NOS Chair: David Schmeltz (USEPA)

Vice Chair: Richard Tanabe (Environment & Climate Change Canada)

Secretary: Melissa Puchalski (USEPA) (nominated to replace Amy Ludtke)

April 10th 2018

1. Approval of minutes from Fall 2017 NOS meeting (San Diego, CA) – David Schmeltz

- Motion: Greg Wetherbee motion to approve; second by Melissa Puchalski. Approved

2. Nomination of new NOS secretary – David Schmeltz

- Amy Ludtke retired from USGS, so a new NOS secretary needed to be appointed.
- Motion: David Schmeltz nominated Melissa Puchalski; second by Richard Tanabe. Motion approved.

3. AMoN update – Melissa Puchalski

- Melissa provided a snapshot of the network
 - There were 96 active AMoN sites.
 - Since the network began in 2007, we now have 10 years of NH₃ concentrations at several sites. Most sites show a flat or increasing trend.
- AMoN quality assurance results were reported
 - Melissa noted the laboratory hood blanks remained low after the increase in early 2017. She requested that Wisconsin continue to monitor and regularly report blanks
 - Variability between the triplicates continued to be low (3% in 2017). Precision reported as coefficient of variation
 - Uncertainty was reported as median (2sigma) using triplicates from previous 3-year period for quartiles. Melissa noted a goal is to add uncertainty values to the database
 - Only one travel blank was above the acceptance limit (0.2 mg-NH₄ L⁻¹) in 2017. Flags should be applied to ambient data below the Limit of Detection calculated at 95% confidence limit using the Currie method.
- Melissa described EPA studies to improve NH₃ deposition estimates and validate concentrations
 - NH_x study was conducted for 6-months over the summer months in 2017. CSN and IMPROVE samplers were co-located with Annular Denuder Systems (ADS) and AMoN in Gainesville, FL and Duke Forest, NC. CSN and IMPROVE utilized a phosphorous coated filter to capture NH_x to determine if sites could easily measure NH_x using existing equipment and infrastructure. Results are preliminary. AMoN was biased high against ADS at Duke Forest and low in Gainesville. Comparing 2-week integrated sample (AMoN) with 1:3 day ADS.
 - AMoN Site Characterization study is being conducted at Chiricahua National Monument (AZ98), Bondville (IL11) and Duke Forest (NC30). Soil and vegetation chemistry and characteristics are being collected seasonally to parameterize bi-directional flux model.

Goal is to decide what measurements can be modeled or plugged into the model from the literature to calculate a site-specific flux at AMoN sites. Field portion of the study will be completed in Summer 2018.

4. AMNet update – Mark Olson

- Mark provided a snapshot of the network and described the network for those that may not be familiar with AMNet
 - There are currently 19 AMNet sites, but 2 questionable sites (OK99, ME97). These two sites haven't submitted data in a few years and they are not paying the annual AMNet fee. Both sites are suffering from staff turnover, but equipment is still at the site. One site (UT97) closed.
 - Mark is installing an AMNet site at MN06 for a Tribe Nation
 - There is a lot of equipment available (owned by NADP). Bondville has a speciation analyzer; Clifty Falls has a speciation analyzer; Leach Lake has a speciation analyzer; and Boston has a GEM system.
 - NY20 switched from speciation to GEM and that equipment is available.
 - USEPA MA has an Analyzer+ available
 - UVM has a speciation sampler + analyzer available.
 - Mark noted that he will pick up spare equipment during site visits in 2018 when he is nearby
- AMNet QA and training
 - AMNet site visits have been put on hold in 2018 during the lab/PO transition. Mark completed 12 visits last year.
 - There are other problem sites in addition to ME97 and OK99. MD08 and OH02 didn't have argon during the site visit, so they couldn't be evaluated and IN22 had problems.
 - Some site operators have requested training. PRI management would not approve sending Mark to train operators, but Mark asked the group for their opinions. He suggested applying a fee for annual visits (visits are required and included every 2-years). Mark will bring up these requests with WSLH.
- Data and documentation availability
 - Mark stated that all 2016 data is available on the website and the password has been removed. The 2017 data being reviewed by Mark. Greg Wetherbee noted that he is ecstatic about the password being removed!
 - The 2017 QA plan is almost complete, but needs 2017 validated data.
 - The Data Manual has been updated and includes QR codes, but needs 2537x updates.
 - Evaluation of AMNet Equipment SOP and Operator Manual needs to be reviewed.
 - All documents need updated web urls and new contact information.
- Asia Pacific Mercury Monitoring Network (APMMN)
 - There will be a September workshop and Mark would like to stay involved. Japan wants to run their data through NADP QA program. NADP and Mark's involvement would mean there would be comparable international Hg data.
- New Personnel: a PhD student will be starting June 1 and the back-up site liaison position is opening up

5. Tekran 2537x Report/white paper - Mark Olson

- In 2009 when NADP accepted Tekran's for AMNet, two versions were available (2537A and 2537B). In 2011, the 2537x became available. So, NADP wanted a comparison to the 2537A/B.
- Field Comparison
 - Co-located measurements were conducted at WI07 between 9/2013-8/2014 between 2537B and 2537x.
 - They added another 2537B between 8/2014-1/2015.
 - GEM concentrations were consistent but low (background site) and GOM and PBM concentrations were near detection limit. It was noted that this was a poor comparison because concentrations were so low.
- Laboratory Comparison
 - In the AMNet lab, a 2537A:2537B:2537X were operated between 1/23-1/28 2017 for GEM only while varying concentration in the laboratory
 - Mark ran a second study with 2 of each analyzer between 6/26-7/5 2017 for GEM only while varying concentrations.
- Environment Canada was also testing the 2537x with the A/B systems. They found +10% bias with the 2537x. NADP did not see this bias in the lab or the field. Both datasets are included in the white paper.
- A motion passed at a previous meeting to grant approval to use the Tekran 2537x CVAFS automated Hg analyzer for use at AMNet sites.
- Mark discussed the status of the white paper (in progress)
 - Mark and Tim Sharac have taken the lead. Tim wants to perform more statistical analyses.
 - Mark asked what the final product should be and what data should be included?
 - Greg Wetherbee suggested a publication in Environmental Monitoring and Assessment (have published Greg's QA study papers).
 - It was noted that Agency reports are a lot of work.
 - To publish the results Mark will need to shorten the report.
 - It's Mark's goal to complete the white paper by the Fall 2018 meeting and publish a journal article in 2019.

6. Site Survey Report - Eric Hebert

- EEMS performs site survey's at NADP's NTN, MDN, AIRMoN and AMoN sites to assess field QA and siting criteria. They also make recommendations on site improvements and make repairs when needed and able to.
- Eric showed a map of the 2017 site surveys conducted. EEMS visited 95 locations which included 80 NTN collectors, 24 MDN collectors, and 3 AIRMoN collectors.
 - The electronic raingages continue to perform very well.
 - The ACM collectors had a few issues with inactivated sensor temperature compared to ambient temperature (AZ97, WY99, CO19 were slow to respond, but may be attributed to operator error).
 - Results from activated sensor temperature increase and elapsed time also showed good results.
- Eric showed a host of problems encountered during the site surveys including:

- Vegetation encroaching
 - Insects/nests
 - Operators not maintaining sites (GA41 fire ants)
 - Rubber boots on arms cracking
 - Dry buckets not kept clean – they should be cleaned at least monthly (every 2 weeks for dirty sites)
 - Dirty lid liners should be cleaned weekly
 - Lid liners should be replaced – NADP relies on the site operator to notify them when they need a new liner. The new Teflon lid liners are more rigid and harder to put in place so seal is poor with bucket
 - Unsafe electrical work
 - Water leaking on to the data logger
- Eric recommends the new PO make site operator training a priority
- **Summary of results found at 2017 surveys**
 - It is common that sites are violating the 30 degree rule for trees. EEMS has not seen improvements in sites that have been visited multiple times. Same with 45 degree rule criteria.
 - EEMS has not seen improvements in dry side buckets being cleaned. There are fewer ACM collectors that require dry side buckets in the network so it is a misleading improvement.
 - Lid seal problems for NCON have remained the same/increased.
- Tom Bergerhouse noted that EEMS should have access to trouble ticket system now. EEMS does not want to be allowed to close tickets, only enter issues/actions.
- Eric believes overall the survey results have improved because of equipment upgrades.
- Camille asked how many Belfort raingages are left and how hard are they to replace. It was noted that the issue is funding for the new electronic gages. Kristi Morris stated that at one point there was funding set aside to purchase new gages, however PRI management vetoed the equipment purchase.

7. Raingage Problems and Improvements to the Network - Bob Larson

- With the transition to WSLH, Bob has taken on a new role of streamlining data processes and field data collection in addition to setting up the database.
 - The transition team is trying to be proactive at addressing field problems affecting data quality.
- There is a system for automatic precipitation screening where flags are applied to data files as they are uploaded, so Bob can examine potential issues.
 - Bob showed table of available flags for automatic screening (potential problems)

Flag	Description	Criteria
X	Excess precipitation	Total precipitation >10", or >0.5" recorded in a single 15-min period
G	Gap	Less than 90% of the expected records were recovered

N	Noisy load cell	Load cell slope changes between positive and negative at least 12 times in any 6-hour period
F	False precipitation	Load cell decreased by 0.007" or more within 2-hours of a precipitation measurement
B	Blocked optical sensor	Sensor blocked for >50% of the time
V	Voltage issue	At least 3-hours of low voltage (<10 volts)

- In 2018 approximately 3000 data samples were screened
 - NOAH IV – 63% no flags
 - Pluvio – 82% no flags
 - Most common flag is artificial precipitation for both gages
- Post screening review includes reviewing datasets graphically. At this stage the reviewer can mark the dataset as good, correct the dataset, mark unusable data, and add comments.
- Corrective actions include working with operators on proper gage assembly.
 - Training videos would help including a Noah IV troubleshooting video for installation
 - Shell swap program: the PO repairs broken shells. They are trying to be proactive by replacing or fixing broken shells to reduce data loss
 - There are other installation issues which leads to sites with chronic noise issues with Noah IV precipitation values. Bob showed graphs highlighting the problem and corrections. Blocked optical sensors even with particle counters cause noise in precipitation data.
 - Collectors being installed on same platform as windshields and/or same platform as gage causing vibrations and noise in precipitation data
 - Recommended solutions
 - Isolate gage from wind screens and other sources of wind induced vibrations
 - Improve deck construction
 - Would dampening help?
 - Would longer-term averaging, optimized for 15 min periods help smooth data?
- Data retrieval
 - PDAs are a common source of problems with site operators. The PDAs are no longer supported by Windows, but they are still used at >50% of the sites
 - Options for replacing PDAs include:
 - Android phones or tablets (\$100+) and use existing Bluetooth adapters
 - Are tablets rugged enough for the field?
 - Ipad/iphone would need wifi transmitter (\$375)
 - Flash drive could be used as alternative replacement but has its own set of issues (may require firmware)

- Cellular telemetry would be more expensive for startup and include a reoccurring cost, but can be purchased through Campbell. Campbell will manage the data. Campbell provides this for free.
- Mark Olson noted that the Program Office has very few spare PDAs because so many have needed to be replaced. The PO has replaced the screens on some.
- Mark Nilles asked what the learning curve looks like for operators switching to Android. There is a one page instruction sheet for switching power; two pages for setting up Bluetooth.
- Greg Wetherbee stated the PO should do what they think is the best option for moving forward. *Action Item: the PO needs to look at durability and cost for each option.*
- Mike Olson asked how many PDA's would need replacing. There are 159 sites using PDAs. It was suggested that instead of swapping with a replacement PDA, replace with an Android/tablet. Greg Wetherbee suggested that the PO buy in bulk, but then maybe have site sponsors buy from the PO. There is a risk for the PO to purchase tablets that then no one would buy. PDAs went through PO because there was so much programming to do before an operator could use them. With Androids it's very easy for operator to start up.
- PDAs were added as a line item to federal bills the year they were deployed.
- Donna Schwede asked if there is an option to have sites lease/buy androids from PO in their "subscription"? Mike Olson replied that he doesn't want to raise fees when they have been saying WSLH would not increase costs during the transition.
- *Action Item: Send a notice in the newsletter that if the operator already owns an Android phone the PO can give you a better option than using PDA. EROS is in the process of developing newsletters.*

8. Collector Status and Improvements - Mark Olson

- Mark discussed how the new PO is emphasizing being proactive with potential field and data issues.
- The PO is focused on training videos and training CAL staff about what happens in the field. Bob is training PO staff on Campbell programs and troubleshooting over next 6-months.
- Automated emails to operators are created to provide operators with warnings before there is a problem to help with data completeness. Bob Larson has created an area to add comments to the database so the PO can note their response when they get the emails.
 - How responsive are operators to automated emails? Mark Olson hasn't sent automated emails – the ones that have gone out were personal emails from Mark. He usually gets a response on Tuesday when the site operator is in the field.
- Upgrade NOAH IV shell wires because they are brittle. Also move away from the PDAs.
- Available equipment includes NOAH IV Shells which are being circulated to repair sensors.
 - The PO will deploy spare equipment where it's needed (i.e. windshields).
 - Keeping some equipment for training staff on-site.
 - Do we want to repair the network or try to expand the networks with spare collectors and gages?
 - Use to repair equipment
 - Get equipment from sites that have been shutdown

- Swap samplers
 - *Action Item: Produce list of equipment at sites that have closed and try to go get the equipment returned to the PO*
- Future use of ACM collectors for dry side studies – is this what we want to do with our extra ACM collectors?
 - Brahney samples – 3 ACMs
 - Likely wants to collocate with her existing sites because she can't get phosphorus.
 - Lad Strzok – parts available
 - Greg Wetherbee said if the PI wants to do something out of the ordinary to a site, then they need to get approval from NOS; if they just want parts it's up to the PO.
 - No point in replacing ACMs with older ACMs. Mark Nilles stated if one of our ACMs break we want to make sure we still have the spare parts and they aren't all loaned out.
- Mark asked if they need approval to post troubleshooting guides on the website? Greg Wetherbee responded that you don't need approval. If you want to ask someone to review that's fine but you can post to the website when they are finalized. *Action Item: The PO will begin to post the troubleshooting guides.*

9. Discussion about Madison Supersite Capabilities - Mike Olson

- Mike provided NOS with potential options for an outreach site near the PO/lab with the possibility of adding a flux supersite further away to meet siting criteria.
- Objectives of adding a site:
 - Add to network data (fill in spatial gaps)
 - Outreach and visibility
 - Training personnel and a new PO
 - Quality assurance
 - Assessment and comparisons study of analytical results
 - Assessment and comparisons study of equipment and methods (cost efficiencies)
 - Research expansion and method investigations (sensors, new analytes, ecological impacts)
- What are the needs/criteria?
 - Accessibility to the PO
 - Existing NADP sites aren't necessarily accessible to Madison PO
 - Collocated with existing aerosol sampling done by the University
 - Representative of network
 - Low-cost
 - Access to operators
 - Students, volunteers, seniors, etc
 - Physical setting – power, security, expandable, platform, shelter
 - Meeting siting criteria
 - Vid Grande asked if it is okay to put a site in Madison because most of our networks are in rural areas? Greg Wetherbee responded that this brings us into the future with urban monitoring.

- The goal is not to have a site that doesn't meet the siting criteria, but it will provide an interesting data set to compare to nearby rural sites (Horicon).
- Mark Nilles noted that NADP has always had urban sites but they are noted as not regionally representative. He would vote for a site near the program office over a site that no one will visit.
- John Walker recommended that if you do want to look at dry deposition the siting criteria will be very important so it really depends on the question and the answers and may require the PO to look at multiple locations.
- Mike described potential options including:
 - UW Arboretum which has a historical record of ecological research. It is a good location for outreach and visibility. The site is under ecological restoration. There are golf courses to the west of the arboretum. They already have precipitation gages. Staff at the arboretum would put interactive displays inside to talk about the site.
 - USFS Product Research Lab is more urban. This site wouldn't meet any siting criteria but they have equipment and are a good partner. The location is secure.
 - WDNR service center – next to wastewater treatment plant, and industry nearby that could influence results. Mike has not contacted anyone at DNR yet.
 - Others include area technical colleges; college of Ag and Life Sciences locations; Horicon WDNR site; Mark Olson's farm
- Potential capabilities would include:
 - All networks and litterfall
 - Atmospheric measurements for understanding dry deposition
 - Mike is interested in black/brown carbon
 - Gas phase nitrogen, PM, SO₂
 - Sensor arrays – is this the way of the future once precision has improved? Other low-cost methods?
 - Research equipment – raingages, bag samples, semi-continuous analyzers, etc. They could leverage NADP equipment and infrastructure to get into future research areas
 - Ecosystem research
- Discussion
 - Devil's Lake is approximately the same distance as Horicon from Madison, but would meet siting criteria
 - Low-hanging fruit is arboretum, but the location proposed is problematic because of surrounding trees.
 - Potential dust from vehicles – parking lot
 - Mostly foot traffic right next to site
 - Haven't discussed how they deal with ice on sidewalks, etc. in the winter

April 11th 2018

10. USGS External Quality Assurance Report - Greg Wetherbee

- External quality assurance program has been run by USGS since the beginning of NADP. Greg has been leading project for 16 years.
- He is currently running the Co-located sample program for NTN only. He hopes to add MDN in the future, but it will be very expensive.
 - 11CO/CO11 co-located N-CON collectors
 - Catch – one collector collects slightly more the other but nearly identical
 - Analyte concentrations – one collector was slightly higher for conductance and cations but this can be a result of higher catch.
 - Results are similar to last year with a 5-10% absolute difference in annual fluxes.
 - The 2015-2016 report will be out soon.
 - MDN results – Frontier Eurofins results were good – no biases
 - Greg showed the control chart for Frontier Eurofins (10 labs participating providing most probable total Hg concentrations). No bias in results.
 - WI Hg lab had a slight negative bias
 - Taiwan's lab had strong negative bias previously. Mark Olson visited lab and results improved. Some negative biases in Jan/Mar 2017 but then improved again.
 - Frontier had no blanks outside acceptance limit.
 - Greg explained System blanks. The USGS sends DI water to the sites and after a dry week operator pours half blank in collector and sends what's in the collector and what's left in the bottle to Frontier to determine contamination. Results are shown for 3-year rolling averages. Max contamination has been near 0.1 ng/L Hg for MDN.
 - NTN results – all results were good for I-CAL.
 - Greg showed the control chart for I-CAL. Solutions were sent to 9 labs from USGS. NH_4^+ was within statistical control. NO_3^- had 1 sample out of control. SO_4^{2-} had 1 sample out of control (same solution as nitrate).
 - I-CAL had 2 blanks (DI water) with detections for K^+ and NH_4^+ .
 - For system field blanks, USGS sends DI water and synthetic rain solutions to operators. 75% of the solution goes into the collector, sits overnight and then the operators ships both the remaining solution in the bottle and the sample added to the bucket to the CAL. Max contamination for NO_3^- was near 0.1 mg/L. and contamination was lower for the other analytes.
 - Loss of analytes continues to be very low for NH_4^+ and NO_3^- .
 - Greg's publications
 - 2015-2016 external QA report (in preparation for publication)
 - Data release for Br trends paper in final approval stage

- Contributing 3 chapters to TDEP white paper (moving forward)
 - Urban deposition for STOTEN special issue (will be submitting article)
- Greg has also been leading the laboratory transition team which included:
 - Pulling together and implementing the Readiness Verification Plan
 - Spiking/preparing samples for analysis by WSLH and other labs to ensure comparability
 - Data analysis for Readiness Verification Plan will be submitted to QAAG
- Eric Prestbo noted that QA is important and recommend putting a QA tab next to the Data tab on the NADP website. Greg has a website with QA data that is overdue for an update to occur this summer.
- Donna Schwede asked that we include QA in newsletters including results of the Readiness Verification and how things are going
- Mike Olson recommended that for fall meeting Greg should highlight trends in QA over the past 40 years. Greg will do a poster and a half page summary in the annual report.

11. CAPMoN Update - Rosa Wu (Environment and Climate Change Canada)

- Currently 34 CAPMoN sites operating in Canada. Higher concentration of sites are located in southern Ontario. They are operating 6 MDN sites , 3 AMoN sites, and 1 NTN site.
- Rosa provided an overview of laboratory activities in 2017.
 - ECCC analyzed 6500 precipitation samples and 6800 air samples.
 - Nylasorb filters used for SO₂ and HNO₃ concentrations were discontinued and MTL filters were phased in. Environment and Climate Change Canada has coordinated with CASTNET on replacement. Both ECCC and Amec (Wood) have shared a lot of inter-comparison data.
 - ECCC Laboratory will continue to work with MTL on washing protocols; the lab is also testing breakthrough of 24 hour samples using Perm tubes and gas calibrators.
- Xancom, Inc. was awarded a contract to deliver 16 precipitation collectors (D400) by March 31, 2018. An additional 10 collectors will be procured each year over the next 2 years. Testing is being performed at Egbert.
- CAPMoN is considering going to weekly samples instead of daily. Some sites are already sampling on a weekly basis. Inter-comparisons are being performed at Algoma, ON and Jackson, NS to compare: open/close times, precipitation weight, and precipitation chemistry.
 - Results of open/close testing-> 3% difference at Algoma (1.4% difference in sample weight); 9.6% difference and Jackson (1.3% difference in sample weight).
- Egbert special inter-comparison study
 - Comparison of C300 vs D400 (11/1/2016-1/2/2018)
 - Weekly versus daily samples
 - Results – C300 vs C300 1.9% difference in open/close; D400 vs D400 3.1% difference; C300 vs C400 15.4 difference (D400 stays open longer than C300).
 - D400 higher than C300 in sample weight (0.2-1.5%); daily composite values 2.1-3.4% higher than weekly values.

- Changing to D400 and weekly sample results in 1.5% difference than current protocol (daily) with C300.
- Next steps include testing sensors for open/close times.
- Data is available: <http://open.canada.ca/en>

12. CASTNET Update - Melissa Puchalski

- Melissa provided background on the CASTNET network and then a snapshot of the research that EPA/CAMD is actively participating in related to dry deposition.
- CASTNET was designed to report on long-term sulfur and nitrogen trends to provide accountability for EPA's emission reduction programs. The network has evolved and now provides regulatory O₃ measurements, supports model evaluation/development and provides a platform for ecological and deposition research.
- CASTNET is operated by EPA, NPS, BLM WY State Office with support from many other partners.
- CASTNET is funded through an appropriation, and funding is applied to the base program, research and development, NADP and the independent QA programs.
- There are 96 CASTNET sites currently. All filterpacks are prepared and analyzed by the Amec Foster Wheeler (now Wood) laboratory. Additionally, 80 sites measure O₃ and 7 sites measure trace gases.
- In 2012, CASTNET developed a small-footprint, low-power site that has been installed at 7 sites to fill in spatial gaps. Three of these are tribal sites. These sites are better suited for special studies or sites in remote locations where power may be an issue or a shelter would be cost prohibitive.
- CASTNET has now fully adapted the TDEP hybrid method for reporting dry and total deposition. This means trends now only go back to 2000. The historical MLM provided point estimates within 1-km of the CASTNET site. Site estimates using the TDEP method will be calculated using 9, 12-km grids around the site. The trends remain the same, but there is a shift in the total deposition because TDEP includes NH₃ and unmeasured N pollutants.
- EPA CASTNET sites were upgraded to regulatory compliant monitors in 2012. The data are submitted to EPA's Air Quality System (AQS) to support the O₃ NAAQS. CASTNET provides a unique dataset because unlike SLAMS sites, CASTNET sites are located in rural areas, at high elevations, are well positioned to capture impacts from wildfires and O₃ transport.
- Eight CASTNET sites measure total oxidized nitrogen (NO_y). CASTNET compares NO_y to total NO₃ (NO₃ + HNO₃) which provides an estimate of unmeasured oxidized nitrogen.
- Nitrotrain was designed using an existing NO/NO_y system. It is a 5-channel system with solenoid switching between channels every few minutes to provide hourly estimates of NO, NO₂, NO_x, HNO₃, NH_x, NO_y, and TN_x using one detector.
- EPA's Office of Air Quality Planning and Standards (OAQPS) designed a 6-month study in the summer of 2017 to determine if existing networks (CSN and IMPROVE) could capture NH_x using an acid-impregnated filter. CASTNET co-located the CSN Super SASS, IMPROVE PM sampler, URG Annual Denuder Systems (ADS) as the reference method and a CASTNET filterpack/AMoN for integrated sample comparisons at a site in Gainesville, FL and Duke Forest, NC. Samplers were operated on a 1:3 day schedule. Preliminary results indicated that the IMPROVE sampler captured NH_x with a slight positive bias and CSN showed poor results at both sites.

13. Low-cost method for time-integrated dry deposition measurements - John Walker

- John described a modified COTAG measurement system and his plans for testing the system over the next year. This would provide TDEP and modelers with improvements to the dry deposition estimates.
- Direct dry deposition measurements are expensive, generate a lot of data, and systems are difficult to operate.
- Deposition community needs to start thinking about low-cost, long-term direct deposition sites in network mode to compliment intensive studies at a small number of sites. The system needs to be optimized for spatial coverage to develop deposition budgets. This system is not designed for process-level research.
- What are the needs for network deposition sites?
 - flux approach must be physically sound – need micrometeorology
 - relatively low-cost
 - suitable for routine network operation (site operator visits once a week)
 - suite of compounds measured at same time
 - continuous measurements of multiple compounds is not suitable for a large number of sites
- There are a few options for network direct deposition measurements.
 - time integrated measurements – denuder/filterpack
 - gradient measurement configuration
 - COnditional Time Averaged Gradient method – (COTAG) combines time-integration and gradient methods
- Direct flux measurement using traditional aerodynamic gradient approach use micrometeorology; the flux is proportional to gradient.
 - Time integrated measurements:
 - typically measure gradient over 30 min - 1 hr
 - John proposed to test this method over 1-week or longer at Duke Forest, NC
 - Method was originally designed for SO₂ and NH₃ by CEH Edinburgh
 - Conditional sampling:
 - Must measure the stability of atmosphere which changes during day/night. Typically have unstable conditions during the day.
 - Concentration gradient is high at night during stable conditions.
 - Averaging gradients over long periods would bias the fluxes due to large gradients during stable periods.
 - Instead you must sample over long periods during specific (conditional) stability conditions.
- Prototype of the COTAG system includes a sonic anemometer, relative humidity sensor, precipitation sensor, soil temperature, soil moisture, surface wetness, and four sample boxes (2 at 2 heights or 3 heights with one duplicate).

- System is designed to measure concentrations on different channels within each sample box based on stability (neutral stability, slightly unstable, slightly stable, dead band) – conditional sampling.
- System can also look at upslope/downslope (i.e. at Rocky Mountain National Park).
- System was based on design for DENuder for Long-Term Atmospheric sampling (DELTA) used by UK – glass denuder/filter pack system. DELTA is used for routine monitoring. Low-flow system can be used for monthly sampling.
- Each sample box contains 4 denuders (2 basic and 2 acid-coated in series), plus a 3-stage filterpack.
- What are the limitations of conditional time-integrated sampling?
 - The system only samples a concentration gradient during conditions that satisfy micrometeorology flux framework. The system won't provide continuous measurements.
 - The stability window must be narrow to avoid large concentrations which would bias the gradient. The stability corrections are nonlinear and vary by site. This method will miss data with narrow stability conditions, but reduces overall bias.
 - At Duke Forest the poorest temporal coverage occurs at night during stable conditions. At night is when the fluxes are low – most deposition happens at night.
- Next steps for prototype testing:
 - Validate chemistry during spring-fall 2018 including evaluating coatings for the denuders and assessing the precision of the denuders and filterpacks.
 - Testing the flow system – precision across the channels (ongoing).
 - Setting up the micrometeorology/data acquisition systems (spring/summer 2018).
 - Measuring the flux accuracy and detection limit (2018-2019). John will do this by comparing the COTAG to the MARGA flux system.
- Cost of the system for network-mode
 - \$25K for prototype developed by EPA/ORD
 - Includes 40 sets of denuders/filterpacks
 - Analytical cost for 2-week sampling + blanks
- Site requirements
 - AC power (modification could do solar)
 - Operator
 - Suitable fetch (flat, homogenous surface to distance of 100x sampling height)
 - Windy sites (better for conditional sampling – meets criteria more often)
 - Above forests would be difficult (windy and rough but small concentration gradients).

14. Applications of MARGA to supplement monitoring network data - Greg Beachley

- Greg provided an overview of the MARGA sampling system. MARGA 1S measures hourly concentrations of gases and particles using an in-line IC. MARGA can also be set up to measure concentration gradients (MARGA 2S). In this mode two sampling boxes measure concentrations at 2-heights.
- EPA's ORD has built weatherized shelters for the sampling boxes so they can be deployed outside of a temperature controlled shelter for the 2S gradient system. The weatherized boxes have been installed on a 38m tower at Coweeta, NC and at a Charleston, SC site over a grass field at ~2m.
- The MARGA 2S direct flux system was evaluated for accuracy and precision by Ian Rumsey (previously EPA/ORD).
- Why does EPA continue to deploy MARGA?
 - The multi-species hourly measurements help to validate and understand integrated network measurements from CASTNET and AMoN.
 - Improve information on pollutant speciation and deposition to develop more complete nitrogen and sulfur budgets.
 - Investigate pollution events on an hourly time-scale and provide direct deposition fluxes and deposition velocities to develop model algorithms.
 - Expand research to different types of ecosystems.
 - Develop a public database.
- Deployments and available datasets from concentration systems:
 - Bondville, IL (2017) and Beltsville, MD (2013-2015) – co-located with CASTNET and AMoN. Operated by EPA/OAP.
 - Theodore Roosevelt National Park, ND (2013). Operated by CSU.
 - Rocky Mountain National Park (2013). Operated by CSU.
 - Eastern Shore, MD (planned 2018). Operated by USDA – weatherized sampler on a dock.
- Flux measurement intensives:
 - Duke Forest, NC over a grass field (2012).
 - Coweeta, NC over/within a forest canopy (2016).
 - Charleston over coastal grass (2017). The research group had no experience with MARGA. Greg was able to assist with troubleshooting and operators changed solutions and ran calibrations.
 - Duke Forest, NC over forest canopy (2017).
- There are currently 2, 2-S systems available for special studies.
- Greg showed usability of data: method comparison (comparison to AMoN, CASTNET filter packs), flux of gases and particles.

15. Quantitation and speciation of total soluble reactive phosphorous: inputs from precipitation and dust deposited along a latitudinal transect in Newfoundland and Labrador - Trevor VanderBoer

- Sources of atmospheric soluble reactive phosphorous (SRP) include anthropogenic sources and natural sources. Phosphorous can be deposited through wet or dry deposition processes.

- Atmospheric presence of SRP is dominated by emission and deposition of coarse mode aerosols.
- SRP can represent a limiting or co-limiting biological nutrient with reactive nitrogen – ecosystems may shift to P-limited where nitrogen deposition or availability exceeds that of phosphorous.
- Transects in North American SRP span periods of weeks but this does not capture the temporal variability in atmospheric transport and biological activity.
- NADP and AIRMoN are the only continuous measurements of SRP in the US.
- There is a need for SRP measurements in boreal ecosystems as it affects the biological activity and help predict climate feedbacks.
- How do you link atmospheric inputs of SRP to boreal ecosystem responses using a latitudinal gradient?
 - Research group drove across the latitudinal transect in 2011 to quantify terrestrial C-storage and cycling
 - Objective was to capture atmospheric inputs continuously from 2014-2016 that may impact boreal growth through C-storage and cycling, capture seasonal and latitudinal trends in speciated gases, particulates, and precipitation inputs and exchange and then link these inputs and trends to ecosystem stocks and fluxes.
 - Developed a sampler prototype to capture wet/total deposition. Everything is run with solar and/or battery packs. The automated wet deposition samplers are deployed in triplicate. Biocide is used to fix samples against microbial transformation during transport. Three measurements are made: openfall, throughfall and static. Dry deposition is calculated as the difference between openfall and static.
 - PO_4^{3-} is measured by flow injection analysis coupled with UV-VIS colorimetry; Total Dissolved P (TDP) is quantified by ICP-OES;
 - They minimize error through extensive QA/QC procedures including standard additions and calibrations
 - Organic phosphorous calculated from total – inorganic phosphorous
 - They found that SRP decreases with increasing latitude with a much larger contribution from inorganic P than organic P.
 - They also found that SRP fluxes increase in summer with the highest fluxes realized in the fall. They see the same pattern across all sites and trends are consistent between 2015 and 2016.
 - Fluxes range from $0.13 - 3.6 \text{ kg P ha}^{-1} \text{ a}^{-1}$.
 - Coarse mode dry deposition dominates TDP transport to transect.
 - Dry deposition fraction decreases with increasing latitude.
 - Measurement data compare well with modeling results for total P deposition.
- Sahara is major global source of P-bearing coarse mode aerosols.
 - HYSPLIT back trajectories showed increasing deposition from NW or potentially from North American/Arctic dust.
 - There is correlation between Total dissolved P versus total dissolved N across the transect.
 - Southern regions may be more sensitive to P input because of nitrogen availability.
- Continuous measurements of total dry and wet deposition of P showed seasonal increases from summer through fall across the transect.

- Driven by dry deposition (largest contribution to total). Dry deposition magnitude of total SRP decreases with increasing latitude. Wet deposition is similar across sites.
- Annual quantities compare well with range estimated by coarse mode phosphorus emission and atmospheric transport models.

16. Bottle change for MDN - Ryan Nelson, Eurofins Frontier Global Sciences, Inc.

- This discussion began at the Fall 2017 NOS meeting. The HAL compared glass bottles to PETG bottles. Results of catch and Hg concentrations were shown. The PO sponsored comparison for 3 sites for 3 months (WA18, IL11, WI31).
- Site results showed good comparison, but the discussion led to questions about cost when moving to PETG.
- Advantages to change to PETG include:
 - The bottles are testing clean out of the box;
 - PETG bottles have been used by Frontier for 4 years;
 - PETG bottles will not break during transit, and there will be fewer leaks;
 - PETG bottles will fit in current sampling systems;
 - The need for bottle blanks can be minimized/eliminated as PETG will be Lot-sequestered
- Disadvantages include:
 - PETG bottles are one time use bottles (added cost):
 - This results in an increase in waste, but cleaned bottle is recyclable;
 - A modified cap is needed for MDN collector sample train connection to 2L PETG bottles, however a modified cap is not needed for a 1L bottle;
 - The fit with thistle tube is just as good/bad as with current glass bottle:
 - The 2L PETG bottle is \$10/bottle, \$4.5 for 1L
- Frontier plans to shift to 1L PETG bottles (will reduce cost, will hold 4" of rain – covers 98% of sample volumes collected from current MDN sites. They will keep high rain sites with 2L bottle and will cover 99% coverage).
- PETG bottles still need to be shipped in coolers because of thistle tube/sample train (glass).
- By recycling PETG single use bottles, they will not need to do acid vat washing.
- The analysis costs will remain the same.
- Motion by Greg Wetherbee: Move to accept use of PETG bottles for MDN per the protocol that was presented provided that we allow a seasonal switch to 2L bottles for certain sites. Second by Mark Olson. Friendly amendment included. Motion approved.