TDEP Committee Meeting, October 24, 2014, Indianapolis, Indiana

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1. **Welcome and Introductions**
   Self introductions by all attendees

   Presentations outlined below may be posted on the TDEP web page: http://nadp.sws.uiuc.edu/committees/tdep/ Please refer to the presentations for further information beyond what is provided in these minutes

2. **Status of TDEP Maps and Future Plans** (Presentation by Donna Schwede and Gary Lear)

A. The presentation covered
- Review of what has been accomplished thus far
- Incorporation of new CMAQ runs (CMAQ v5.0.2 bidirectional series)
- Discussion on "Next Steps": What direction(s) does the group want to take TDEP next?

B. Current Status of Maps and Data
- 2014.01 maps and data for 2002-2012 are available from CASTNET ftp site (ftp://ftp.epa.gov/castnet/tdep/) and NADP web site (http://nadp/sws.uiuc.edu/committees/tdep/tdepmaps/)
- 2014.02 will be available by November, 2014 and will include
  - Maps and data for 2000-2013
  - Updated monitoring results for CASTNET, NTN, AMoN
  - Addition of SEARCH particulate monitoring data
  - Does not include any new model runs
- AE journal article describing methodology and results available from NADP web site as well as from: http://dx.doi.org/10.1016/j.atmosenv.2014.04.008. The reference for article is: Atmospheric Environment, Vol. 92, August 2014, pp.207-220
- Gary Lear keeping change log of the versions. Included in the documentation. Will post all versions on web site in case there is interest in earlier versions

C. Near Term Plans
- Uses CMAQ v5.0.2
  - 12 km grids for all years
  - more consistent emissions and land use
  - bidirectional ammonia
  - lightning NOx
- AIRMoN data will be added in for Bondville and other collocated sites
- Account for autocorrelation between concentrations and deposition velocity
  - Discussion: Bob Vet noted that this will be akin to adjusting monitoring data with model results instead of the other way around.
  - Zhang commented that not every species is the same. Some autocorrelation results in overestimation, some in underestimation
  - Artz wanted to know how much confidence is there in the results for coastal areas with response from Lear that the hybrid approach does not treat coastal sites any differently which is in line with NADP
- Model will be used to estimate particle size distribution instead of the 80/20 rule
  - CMAQ uses modal model ; CASTNET has no size cut

- CASTNET uses the 80/20 rule which assumes
  - pSO4 is all accumulation mode
  - pNO3 is 80% accumulation, 20% coarse mode
  - pNH4 is 80% associated with pSO4, and 20% associated with pNO3
- CMAQ v4.7.1 versus v5.0.2
  - Layer height
    - First layer is 20 m instead of 38 m. This means that Ra is calculated with a reference height of about 10 m
    - Concentrations and Vd will be different
    - Flux should be similar as still in the "constant flux" layer
    - Bias should be less since first layer is closer to measurement height for CASTNET
  - Bidirectional for NH3: Some areas will show emission when they used to show deposition
  - Mesophyll Resistance - now based on Henry's Law which will have particular impact on NO2 Vd
  - Land use will be NLCD/MODIS 40 category
  - Land-water mask is newer version of the met preprocessor; some grid cells that were treated as water cells will become land cells
  - Emissions are always being updated
    - Lightning NOx included as a source
    - Updated NH3 agricultural emissions
    - Artz wanted to know if satellite data are being used and Denis replied that they are used in diagnostic way such as identifying CAFO emission profiles, but no used in model. Waiting for the 2018 launch of Air Quality Satellite
- How should we do the data fusion for NH3?
  - Fusion of bidi Vd for NH3 with AMoN will be difficult since simple bias correction cannot be done. Much discussion generated with main conclusion being that the end deposition is what is important from an ecological perspective. Denis commented that "bidi" needs to be torn apart in that we need to look at how CMAQ reports the outputs and whether it is a net flux and needs to be split into emissions and deposition

D. AMoN Spatial Variability Study
- Objective is to determine how representative an AMoN site is to any site within a 72 km radius
- Will be conducted at Bondville, IL(IL11) and Fort Collins, CO (CO13)
- Will operate on a reduced sampling schedule (2-week sample every 6 weeks)
- Will validate/evaluate inverse distance weighting (IDW) distance used for TDEP

E. Future Plans
- Incorporation of AMoN variability study results
- Characterizing uncertainty
- Extend estimates to before 2000
- Further model evaluation/intercomparison work
  - Coweeta
  - Intercomparison of CMAQ/CAMx/AURAMS for 2009 (ROMANS II)
- Incorporate Canadian data (availability, PRISM issues)
- Incorporate 1-in-3 networks (IMPROVE, CSN)
  - these networks are only covering 14 to 40% of monitoring week; current criterion is for 75% completeness of week

- could construct 1in3 grids and weight them based on percent of coverage versus continuous
- use weekly concentrations and weekly fluxes
- bias correct on a seasonal basis

- Urban: currently not using any urban monitoring data, but modeling data does
- What issues should TDEP address next?
  - Monitoring Needs Workshop?
  - Other intensive field studies?
  - Revisit Needs Table?

3. **Update from Ad Hoc Committee on Independent Review of a Mercury Dry Deposition Estimation Method** (Eric Prestbo)
   Proposal presented in white paper presenting Leiming Zhang's method to estimate weekly average deposition velocities for gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particle bound mercury (PBM)
   - Three reviewers; only evaluating model, not the quality of measurements
   - PBM: All three reviewers agreed that the proposed approach was valid and acceptable for estimating dry depositions for PBM
   - GOM: Two reviewers found the approach valid and acceptable. The third reviewer said it was unclear because experimental verification was not done for resistance terms or deposition flux and that re-emission probable
   - GEM: One reviewer found the approach valid, second reviewer said it was unclear as the variables were assumed and not experimentally verified. Also that the compensation point was not verified over multiple surfaces. The third reviewer was unsure because net deposition fluxes may be too large
   - Discussion generated. Donna and John made a point that some of the comments about resistances broadly apply to all inferential models
   - If decided to go ahead with proposal the start date for depositions will be 2009, product will be delivered monthly
   - Mae Gustin will provide Leiming with results of her latest research which involves back calculating deposition velocities based on direct measurements which were conducted at three locations
   - A motion was made by Eric and seconded by Gary Lear and approved by all.
     The motion as stated is: TDEP supports the work of Leiming Zhang and the contribution from Environment Canada to generate and deliver to NADP average weekly Vd for GOM, GEM and PBM for the AMNet sites as proposed in white paper. To be delivered with a list of caveats.
     1. This works helps the modeling community to test the deposition schemes implemented in their models;
     2. Moving forward with this work would stimulate further evaluation, research and model comparisons;
     3. Notwithstanding all the uncertainties, it would be useful to have dry deposition estimates for the AMNet sites and the future capability to recalculate depositions as new knowledge becomes available;

4. **Using Isotopes to Help Understand Deposition Sources and** (Presentation by Emily Elliott)
   - Presentation is a compilation of work from the past 5 to 6 years
   - Work was funded by NYPA, EPRI, and NSF for the most part
   - Isotopes vary in the number of neutrons in the nucleus which creates a very

small difference in the mass of the atom

- This small difference in mass causes different reaction rates
- The most abundant form of N is N14; this work looks at N15
- N isotopes were initially used to look at sources of contamination in ground water and the question was whether the same principles could be used to fingerprint atmospheric N deposition
- Investigation started with snowpack samples as a lot of volume is needed to get enough mass
- Recent microbial techniques, developed by Danny Sigman, have transformed the scientific power of isotopic analysis. Denitrifying bacteria are used to convert NO3 to nitrous oxide gas and then analyzed for isotope ratios of this gas. The bacteria are cultured in the lab, and 80 samples can be analyzed per day
- Before this there were poor constraints on N15 ratios in rain water
- This research looked at
  - N isotopes in NTN samples
  - HNO3 and pNO3 from CASTNET
  - Power plant stack gas emissions
  - Passive sample eluents for both HNO3 and N2O
- Denitrifying method was coupled with a bromine oxidation method to look at N15 values of different NH3 sources. With this method as much sample was not needed by orders of magnitude
- Current study is looking at N15 in NH3 in passive sample eluents at 9 AMoN sites where different NH3 source contributions were expected
- 2007 study used NTN archive samples from 2000 and looked at spatial and temporal variability in rainwater and NO3 in northeastern US. Highest N15 values were found in Ohio and values were higher in winter. Can correlate these findings with proximity to power plants
- 2009 study yielded similar results for CASTNET HNO3 and NO3 samples. Temporal variations in N15 were partially controlled by the stationary source NOx emissions. There has been some difficulty in interpreting results due to little information in N15 sources and transformations
- Influence of biogenic NOx emissions can be seen in continental scale maps of 2000 data which show spatial as well as temporal differentiation
- Rates of soil NOx emissions are controlled by a combination of soil temperature, texture/porosity, soil N content, and soil moisture content
- There is a correlation between N15 and fraction of biogenic NOx emissions surrounding each site; the greater the NOx emissions, the lower the N15 values
- There are concerns about the accuracy of bottom-up soil emission inventories
- Isotope analysis and concentrations were used to estimate 20 percent NOx in some areas
- Felix et al's (2014) work looking at different emission sources for NH3 showed that the N15-NH3 values from cornfields and other agricultural sources were very negative. Power plants were generally higher than agricultural measurements
- Transect results show that N15-NH3 can complement concentration measurements to show sources
- In conclusion:
  - isotope information is a strong complement to concentration data
  - yields important source information; otherwise this is difficult to ascertain
  - Need further work to characterize sources. We are at the beginning of the curve

5. **A Plethora of Proactive, Synergistic & Collaborative Reactive N Activities** (Presentation by Bret Schichtel)
    - There are changes in NO3 and NH4 wet deposition (Lehmann and Gay, 2011); NO3 is going down and NH4 is going up
    - Over the last 20 some years there has been a shift from oxidized N dominated wet deposition to reduced N dominated wet deposition
    - Day et.al's (2012) work shows that NO3 and SO4 depositions are going down while NH4 is going up; ammonia gas is becoming more important as there is increased deposition of this
    - Sources of interest are moving from fossil fuel combustion to agricultural emissions
    - At Grand Teton 28% of total deposition is attributed to dry NH3, at Rocky Mountain 17% of total is dry NH3, and 15% at Yellowstone
    - Yi Li et al (2013) compiled AMoN, CASTNET, SEARCH and IMPROVE data for concentrations and then for NH3 Vd used 0.7 times HNO3 Vd
    - Their work showed that dry NH3 accounted for 25-65% of the inorganic N deposition which was the most dominant contribution
    - Whereas SO2 and NO pollutant concentrations are projected to decrease over the next 40 years NH3 is forecast to increase
    - As far as the bi-directional flux of NH3 what is important? The change, just the deposition or some fraction?
    - The NH3 gas diurnal cycle at Rocky during the summer months shows a unique early AM peak which is not seen for PM, NOx and NOy. Could this be from re-volatilization of NH3 deposited during the night?
    - When bi-directional model used, NH3 dry deposition goes from the most dominant form of deposition to the most insignificant. Is NH3 the most important thing to consider, does not matter or somewhere in between?
    - Modeled versus measured NH3 concentrations are 180 degrees out of phase. Something is missing in the model. This has important implications for source apportionment.
    - Maria Val Martin's Global Modeling Framework (2014) through 2050 projects N deposition increasing throughout the Rockies. Ammonia deposition is projected to be the major contributor to reactive N deposition fluxes
    - Source apportionment studies show that NH3 is a regional scale issue. For example, at Rocky only 40% of the NH3 is generated in Colorado with California being the second largest contributor
    - At Gran Teton it is a much more local issue as 90% of the NH3 is coming from the Snake River Valley
    - Results from Bakken are showing an explosion in development with episodes of high concentrations of nitrate and NH4. High NOx has been traced to combustion
    - NH3, generated from leaks of natural gas as well as from oil and gas manufacturing activities, combines first with acidic sulfate, then HNO3 to produce NH4NO3 (especially in the colder temperatures). This contributes to atmospheric haze
    - The question posed was: How are we getting so much NH3 in the winter in North Dakota? And can NH3 be used as an effective control measure to reduce haze?
    - At Pinedale, WY (in the winter) Collett's group saw high HNO3 concentration periods with basically no NH3
    - Conclusions were that high time resolution NH3 measurements are needed to

resolve NH3 bi-directionality issues, determine source apportionment and for development of critical loads

- John Walker stated that we need to push for making direct flux measurements as well as needing to collaborate and combine efforts

6. **Southern Appalachia Nitrogen Deposition Study (SANDS)** (Presentation by John Walker)
    - The motivation for this study is threefold:
        1. In order to support the secondary NAAQS the EPA Program Offices need to be able to fully characterize atmospheric deposition exposure for the NAAQS species and to be able to address and incorporate the full suite of species that affect total deposition budgets of these pollutants;
        2. Improved gaseous and particulate flux estimates affecting the NAAQS pollutants are critically needed to reduce uncertainty in setting and implementing effective secondary standards; and
        3. There is also a need to understand the fidelity of the association between air concentrations and fluxes derived from regional air quality modeling tools. There is also an urgent need to develop budgets of nutrient and acid deposition to support critical loads research.
    - The study objectives are to:
        1. Develop speciated seasonal and annual atmospheric budgets of nutrients and acidity in a Southern Appalachian forest ecosystem, with specific focus on reactive N;
        2. Quantify the speciated dry N deposition budget at hourly and annual time-scales using canopy-scale micrometeorological flux techniques with online chemical measurements; and
        3. Direct flux measurements will be used to assess the completeness and accuracy of N deposition estimates derived from other methods such as throughfall, site-specific inferential modeling, and regional chemical transport models.
    - The following issues will addressed through a combination of measurements and leaf to watershed-scale modeling:
        1. What are the seasonal and annual total atmospheric deposition fluxes of N and S within the Coweeta basin?
        2. What are the relative contributions of wet versus dry deposition to total N deposition at seasonal and annual time scales?
        3. What are the relative contributions of oxidized versus reduced N fractions to total wet and dry deposition at seasonal and annual time scales?
        4. What is the relative contribution of organic N to total N in wet deposition?
        5. Do organic N compounds in the gas phase and in particulate matter contribute significantly to the atmospheric reactive N budget?
        6. What fractions of oxidized and reduced N dry deposited to the forest, and cycling within the canopy air space, originate from biogenic versus anthropogenic sources?
        7. Are deposition fluxes at the Coweeta eddy flux tower and NADP station representative of the Coweeta basin?
        8. How do deposition rates derived from above-canopy micrometeorological measurements compare to throughfall measurements and regional chemical transport models?
    - The Coweeta site was selected for this study because the southern Appalachians

were identified as an acid-sensitive region and subsequently identified as an area of focus for a Field Pilot program (FPP). The hydrologic laboratory at Coweeta is a long term research station where forest nutrient dynamics have been studied extensively and it is also a CASTNET, NADP and AMoN site. The site also has an existing walk-up tower for above and within canopy measurements.

- Previous work at site by Novick, et al has resulted in several publications dealing with:
  - Impact of terrain induced micrometeorological patterns on canopy-scale carbon and water fluxes;
  - Characterization of new fast-response infrared gas analyzer for water and CO2 fluxes;
- It has been determined from the Novick, et al studies that when winds are from the southwest the flux footprint is representative of the study ecosystem
- Carbon, energy and O3 flux measurements are ongoing
- N flux measurements to begin in December of 2014 and will continue for 12 to 15 months
- HNO3, NH3, HONO, NO3, NH4, SO2, and SO4 will be determined by aerodynamic gradient and will be collected on a seasonal basis during the winter/spring of 2015
- Passive sampling of HNO3, NH3, and SO2 being conducted at 5 sites across the Coweeta Basin and is collocated with basic meteorological measurements; the sites are stretched out over a distance of 4.5 km from the flux tower with an elevation gradient of 700 m over this distance
- Knowing the isotopic characteristics of the vertical concentration profiles may identify the relative importance of anthropogenic versus biogenic sources of N entering and cycling within the canopy
- As of November 2014 collaborators included:
  EPA/ORD/National Exposure Research Laboratory
  EPA/ORD/National Risk Management Research Laboratory
  EPA/OPA/Clean Air Markets Division
  AMEC
  US Forest Service Southeastern Research Station
  NADP, CAL
  University of Pittsburgh
- Still looking for interested collaborators, especially to measure gas phase organic N (peroxynitrates, alkyl nitrates, and reduce organic N) as well as aerosol organic N (speciated or total.
- Project may also need additional support for throughfall measurements

7. Wrap-up (Gary Lear)

- On agenda for Spring 2015 meeting: How do we start a consortium and how do we obtain funding?
  - Get someone from EPA STAR program to come to a meeting
  - Get Ray Knighton to talk about USDA opportunities
  - NSF – how do we get groups that can receive NSF funding involved in the consortium?
  - CARB? Invite to Spring meeting
- Jason Lynch would like TDEP committee to provide some measure of uncertainty along with the map products which would be useful from a CLAD

perspective

- Gary Lear responded that this would be a significant task in that how would we get someone who is technically able to address the issue? A presentation from CLAD on how the uncertainty would be used and what kind of metrics would be helpful in achieving this task
- Jason said that CLAD needs to clearly define what they are looking for and what they plan to use the uncertainty values for

8. Monitoring Workshop (Gary Lear)

- Where and when?
- Look at monitoring priorities
- Look at other measurements, not just CASTNET
- Give feedback to measurement organizers
- Identify where the greatest measurement uncertainties are
- Get feedback – is NHx the greatest uncertainty at this point?
- Meeting adjourned