TDEP Committee Meeting, April 22, 2013, Madison, Wisconsin

1. Welcome and Introductions

- Self introductions by all attendees (see attached attendance list)

All presentations outlined below are 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. Hybrid Approach to Estimating Total Deposition Using CMAQ and Monitoring Data

(Presentation by Gary Lear)

- The project goals and outputs are to produce total, dry and wet deposition maps for all components from 2000 to present; maps of inorganic N and S; make products web accessible; and provided as ESRI grid outputs
- The main concluding points from the Fall 2012 NADP meeting were:
  1. To investigate the 'range of influence' for HNO3 and NH3;
  2. Inclusion of more measurements, if compatible, from SEARCH;
  3. Adjustment of concentration surface by the known bias, and
  4. To maintain 4 km gridding for wet deposition
- The need for Total Deposition maps are driven by:
  1. Critical loads work
     * Biogeochemical models need long time series
     * CLAD is creating a national critical loads database (FOCUS)
  2. Other environmental analyses, and
  3. Previous analyses have simplified assumptions which were incorrect
- A hybrid approach, using CMAQ as model, to developing these maps is used because:
  1. Need an operational method estimating dry and total deposition without the limitations (3-5 year time lag and uses historical data) of constructing emission and meteorology profiles required for Eulerian models
  2. Actual point measurements most likely more accurate that models, but there are spatial and chemical gaps in the measurements that need to be filled in with modeling
  3. CMAQ is the model we have available with 7 years of data
- Monitoring data used included : NADP/PRISM wet deposition for NH4 and NO3; CASTNET air concentrations for HNO3, SO3, pNO3, pNH4, and pSO4; AMoN for NH3, and SEARCH for HNO3, SO2 and NH3
- CMAQ CDC data used are CMAQ v4.7 for 2002-2006 which incorporate MM5 meteorology and 2002 NEI platform for emissions; and CMAQ v4.7.1 which uses WRF meteorology with 2005 NEI platform for emissions
- **Methodology:**
  1. Calculation of hourly mean, min, max, and standard deviation for Vd and flux for N and S species
  2. Aggregations of CMAQ runs to same timeframe as monitoring data
  3. Estimation of weekly ambient air concentrations using ambient monitoring networks, inverse-distance weighting (IDW) and 12 km grids
  4. Estimation of weekly dry depositions by multiplying concentrations grids with CMAQ Vd to create deposition product grids
  5. Creation of weekly deposition product weighting grids (Wd) by using IDW. Values range from 0 to 1.0; measurement values have greater weight closer to monitors.

6. Merging of weekly deposition products and CMAQ deposition/IDW grids, and
   a) Adjustment of CMAQ dry deposition grids for systematic bias. This step is new compared to what was presented in Portland Maine in the fall.
      - There is a consistent difference between measurements and model results (systematic bias)
      - Seasonal differences in bias are more significant than interannual differences or trends
      - Spring and fall have higher bias, winter lower
      - Bias determined by comparison of measured concentrations with the average CMAQ concentrations
      - CMAQ dry deposition grids adjusted for systematic bias by multiplying the CMAQ deposition by the bias factor
      - Seasonal Bias Maps**:** Average seasonal bias maps for 2010 presented for HNO3 and SO2 as well as unadjusted and adjusted maps for total N and S
      - Conclusion from review of the maps was that bias adjustment makes very little difference.
      - So methodology reverts back to the way things were done previously but using 4 km grids
7. Summation of weekly dry deposition values into annual aggregations for all measured species
8. Addition of the annual dry deposition and the unmeasured species of: HONO, N2O5, NO, NO2, PAN, PANx, NTR
9. Summation of dry deposition and PRISM-adjusted wet deposition from NADP/NTN for calculation of total deposition
      - The above methodology has resulted in better resolution; shown that bias adjustment methodology employed by Lear has made little difference in total deposition of either N or S; and the addition of SEARCH measurements resulted in modest increases in N and S in the Southeast
      - Presentation of list of caveats to be published with the data
      - Next steps to take:
        1. Finalize maps
        2. Publish to CASTNET website by June 1, 2013
        3. Journal article to document process
        4. TDEP committee to promote work on longer term research projects
        5. Account for cross correlation of concentration and Vd for weekly sampling periods

- **Subprojects:**

The following subprojects were compiled during the fall 2012 TDEP committee meeting. Little to no progress has been made on these subprojects and it was decided that a better effort would be made to make some headway on these for Fall 2013 meeting.

1. Testing the range of influence with CMAQ and passives (Robin and John)
2. Switch to 12 km CMAQ Vd's and then fluxes (Donna and John)
3. Move to finer scale of deposition (Rich and Donna)
4. Investigate NO3 Vd (John, Donna, Mike Barna)
5. Better characterization of organic N
6. Intercomparison of CMAQ/CAMx/AURAMS for 2009 (ROMANS II, more AMoN sites) (Donna, Mike, Bret, Eladio, Krish)
7. Research on other forms of Organic N. Review of Clegg and Wexler AE paper that was supported by EPRI (Mike, John)

8. Inclusion of bidirectional NH3
9. One to Five year variation study (George, Gary, Donna)

Discussion: Improvements to bias adjustment methodology were discussed and it was stated that these improvements in determining bias would be explored before June 1st

3. Origin of Reactive Nitrogen in Rocky Mountain National Park
(Presentation by Bret Schichtel)

- Historically, emissions have been dominated by NOx. It is projected that by 2050 emissions will be shifting from oxidized to reduced reactive nitrogen (RN)
- The objectives of the Rocky Mountain Airborne Nitrogen and Sulfur (RoMANS) Study are to:
  1. characterize the atmospheric concentrations of S and RN species in gaseous, particulate and aqueous phases along the east and west sides of continental divide
  2. identify the relative contributions to atmospheric S and N species in Rocky Mountain National Park (RMNP)
- Deposition budget for RN: 55% is reduced N which is predicted to increase
- Source attribution budgets determined from this study show that springtime N deposition is primarily from east of the Park; summer time deposition comes from a more diverse set of sources of which about 25% of NH3 is from local sources
- Study shows that synoptic events cause high concentrations
- Strategy to determine source apportionment makes use of simple back trajectories, frequency of air mass passing over source areas, trajectory receptor models, hybrid models
- Summer diurnal cycles: higher concentrations for NOx, NOy, NH3 and PM1 in the afternoon and evenings. NH3 also shows a small peak in the AM as temperatures rise
- Colorado is starting to look at developing a dynamic air quality study in order to develop an early warning system to predict synoptic events to reduce NH3 producing operations
- Winds most frequently come from the west, but the highest 10% of concentrations are associated with transport from the east; approximately 45% of NH3 concentrations come from the east
- High NO3 concentrations are associated with the Denver area which is south of the monitoring site
- Could not reproduce all of NH3 coming from the east from analysis of WRF meteorology data; meteorology is underestimating transport from the east.
- When transport is from the east it is short term. There is however persistent transport from southern California as well as Oregon and Utah
- On high NH3 days transport is coming from NE Colorado; also southern California and Arizona
- Using a trajectory based source apportionment method (Trajectory Mass Balance (TrMB)) half of the NH3 was estimated to originate with 12-22% from the Northeastern Colorado and the Front range account; 22-32% from Western CO depending on season. However, the wind fields underestimate upslope-westerly transport and contributions from east of ROMO may be underestimated.
- A hybrid receptor model based on CAMx transport and emissions estimated about 55% of the ambient NH3 at ROMO was from Colorado sources with 10-30% (~22% annual average) from Colorado emissions east of ROMO and 12-42% (~33% annual average) from western and central Colorado sources
- Long range transport NH3 was an important contributor to ROMO ambient NH3 concentrations with 35-45% of the measured NH3 from States west of Colorado

- The Hybrid Receptor Model results compared well to measured NH3 concentrations except in the summer when it substantially underestimated levels with respect to actual concentrations. This model used the same wind fields as TrMB and may too underestimate contributions from sources east of ROMO.
- RMNP would benefit from regional reduction in NH3 emissions as large increases in NH3 concentrations are predicted combined with the large influx of people into the region

4. Update on Organic Nitrogen Wet Deposition Work (EPA, CAL, NPS and CSU)
(Presentation by John Walker)

- Project Background: Study conducted in 2009 by NADP and EPA to look at feasibility of measuring bulk organic nitrogen (ON) in weekly NTN samples.
  - Study consisted of a comparison of field methods to characterize stability of bulk ON in NTN samples; characterization of losses during storage after collection and other possible losses from lab protocols; and a scoping study that measured bulk ON in samples from 55 NTN sites over 12 months to see if spatial and temporal patterns existed
- Conclusions from this study were:
  1. At least 40% of bulk ON is lost from standard weekly NTN samples at BVL130
  2. About 10% of bulk ON is lost in daily AIRMoN samples
  3. Post field collection, ON is stable in the lab if refrigerated
  4. Samples should not be filtered prior to analysis and NO2 needs to be quantified to complete the inorganic component
  5. Variability was evident across the 55 sites
- Based on the above conclusions it was decided at the Fall 2012 TDEP meeting that:
  1. More work was needed to assess the variability of ON stability across sites
  2. A low elevation site at Duke Forest and high elevation site at RMNP were proposed
  3. If results show that loss of ON in daily unrefrigerated samples is on the order of 10%, as observed at BVL130, then can potentially proceed with routine bulk ON sampling at AIRMoN sites
  4. When collection of daily samples not feasible, then investigate stability of weekly refrigerated bulk ON samples
- Therefore, goal of this current project was to conduct a 6-month study to further evaluate potential ON losses in daily and weekly samples at a high and low elevation site. Study will compare daily refrigerated and unrefrigerated samples, and weekly refrigerated samples
  - Samples to be analyzed for standard suite of NTN chemistry as well as total N and NO2
  - Based on above results and funding, analysis of total N and NO2 may be added to AIRMoN
  - sites beginning in 2014
- Project Status: Sampler for Duke Forest constructed and deployed; Rocky site not underway due to funding constraints but weekly sampling may be possible; a simpler version of the Duke site collector will go in at Fort Collins site instead of at Rocky
- The Duke sampler is not feasible for deployment at multiple sites
- A much more complicated sampler would be needed to deal with winter conditions
- There are no calibration standards in use to estimate loss of ON; assumption made that losses are minimal if refrigerated immediately upon collection, however, there may still be some immediate loss before sample is decanted into a bottle
- The ‘loss’ issue has been investigated with known standards and was less than 10%
- People still troubled with the sample stability issue

- The Duke sampler does have a refrigerated bath and the collection compartment is air conditioned

5. Bias and Uncertainty of NADP Total Inorganic Nitrogen Measurements
(Presentation by Greg Wetherbee)

- There have been numerous comparative studies involving:
  - collocated sampling between ACM collectors and ACM vs N-CON collectors
- Differences between NTN versus CAPMoN:
  1. CAPMoN uses a different grid sensor
  2. CAPMoN collects samples in a bag; bags are sterile surfaces
  3. CAPMoN samples daily, no filtration
- Results of NTN vs CAPMoN were compared at PA15 and yielded good correlation
- CAPMoN data do have higher N concentrations
- Bias for NO3 is less than 10% but bias for NH3 is about 15%
- Study conducted by NADP Program Office deployed 6 well-defined QA samples in buckets to determine impact of evaporation on NTN samples. Significant NH3 and NO3 loss was observed. For solutions containing nitrogen as NO3 only (no NH4), 100% NO3 loss was detected
- Results of evaporation study prompted an investigation of bag sampling. Initial results are promising in that minimal N loss was observed with the same QA samples
- USGS Field Audit Program investigated contamination of samples from deployment by using audit solution
  - Losses were calculated per 24-hour period
  - NO3 was lost in more humid locations and contamination detected in other locations but was minimal

***** Will new N-CON collectors affect N deposition estimates?

- If network is retrofitted with N-CON collectors there will be a step function of change
- How to resolve this? How much uncertainty is acceptable?

***** Acceptable uncertainty will depend on what data are used for:

- Ecosystem collapse
- Selected resource harm
- When to install emission controls?

***** Results from collocated N-CON vs ACM sampling:

1. Differences were approximately 1.5 kg/ha of critical load of N with still ±25%. Uncertainty for across the country which is not good enough for critical loads work

Discussion:

- Differences between collocated samples show normal distribution
- Gary Lear does not feel that this is a TDEP issue and that TDEP will not be incorporating these differences into maps
- Eladio feels that there should be a caveat therefore of the results
- Cindy wanted to know what will happen when a sampler is changed out at a site. Will data be adjusted? David Gay responded that there will be a record of the change to inform the data user
- Information about the shift in data will be quantified and will be part of the published reports
- John Walker wanted to know if the loss in N was investigated in a way to see if loss was mainly in the form of NH3? John says from his studies when he saw NH3 loss he did not see an increase in N. It looked like N loss was to biomass. John suggested to look at field audit data for nitrification and denitrification processes

6. Bias in Modeled bi-directional NH3 Fluxes Associated with Temporal Averaging of Atmospheric NH3 Concentrations

(Presentation by John Walker)

- Direct flux measurements are expensive, labor intensive and require complex supporting measurements
- It is often necessary to infer fluxes by using atmospheric concentrations , meteorology, and surface chemistry within a suitable air-surface exchange model
- NH3 concentrations are currently measured using passive samplers
- For estimation of site specific NH3 fluxes from AMON data: need suitable model, and supporting data such as soil and vegetation NH4 and H+ concentrations
- The modeled flux estimates will contain errors resulting from inability of the model to accurately simulate the flux and by the use of time-integrated data rather than hourly data to drive the model
- Time-integrated data may also produce error in modeled NH3 flux because of bias in the air concentration at hourly scale as well as due to covariance between atmospheric concentration and other variables
- This study compares seasonal and annual fluxes derived from hourly versus time-integrated air concentrations over a range of atmospheric and surface conditions
- NH3 exchange is bi-directional, i.e. may be emitted or deposited depending on conditions
- The NH3 ‘compensation point’ is governed by the N status and acidity of the exchange surface
- The goals of study are to characterize the bias between hourly and temporally averaged NH3 fluxes as well as to assess the potential magnitude of t his bias in the seasonal and annual aggregate fluxes
- The following scenarios were investigated:
  1. Low soil/vegetation emission potential
  2. Intermediate soil/vegetation emission potential
  3. High soil/vegetation emission potential
- Fluxes derived from hourly concentrations were compared to fluxes derived from 2-week average concentrations at seasonal and annual scales
- Both seasonal and diurnal variability need to be addressed; diurnal patterns vary from site to site and will produce different flux profiles
- Results:
  1. Low emission profile: Negative flux during all periods, low bias, low deposition in winter, higher in summer. Although bias is low (4%), it does vary seasonally
  2. Intermediate emission profile: Slightly higher bias (11%)
  3. High emission profile: Positive flux, bias around 5%
- For unidirectional exchange species the hourly flux is equal to the product of air concentration and Vd, but this relationship does not work for bi-directional exchange species like NH3
- For bi-directional species, bias increases non-linearly as the net flux changes from emission to deposition
- Conclusions:
  1. Use of 2-week integrated air concentrations for a bi-directional flux model results in underestimate of flux at sites where net annual deposition is observed and an overestimate of flux at sites where net annual emission is observed
  2. Biases at annual scale are much lower than biases at seasonal scale due to offsetting larger seasonal biases

- Use of 2-week integrated air concentrations to model NH3 air surface exchange feasible for development of annual budgets

  Discussion:
  - Use of CMAQ as the model is a problem as far as Eladio is concerned. John said that CMAQ would be used only for the temporal variation of fluxes when using 2-week data and also should be used only for annual fluxes.
  - for seasonal fluxes we need to go further. Eladio suggested use of SEARCH data as they have high time resolution NH3 measurements to ground truth this type of work. Can put in high time resolution analyzers at a few key spots to help with the ground truthing.
  - Tom Butler wanted to know how important NH3 emission were in closed canopy forest. John replied that it can be very important but that the emissions are probably not making it out of the canopy. So probably not very important to the ecosystem.

7. The Impact of Deposition Velocity and Concentration Covariance on Weekly Flux Estimates

(Presentation by Gary Lear)

- Methods for this study consisted of:
- Calculating the average covariance for each site and parameter
- Normalizing the covariance to show strength of linear relationship between concentration and Vd
- Comparing the true sum of hourly deposition, product of the weekly averages, and the 'corrected' product using coefficient of variance
- The parameters looked at were NH3, HNO3, SO2, NH4, NO3 and SO4
- SO2 analysis at BEL116 showed that the product of the means is a good estimator of individual pairs only if pairs are independent and random
- When concentrations and Vd are uncorrelated, the product of the weekly means are reasonably accurate
- Next steps in this study are to:
- Compare model results to hourly measurements from MARGA, hourly SO2, and biweekly AMoN concentrations
- Include bi-directional Vd for NH3 from CMAQ v5?
- Next iteration to be based on CMAQ 0708 runs. Total deposition maps will be corrected using results from these runs
- Comment from Leiming that Tilden Meyers has done similar work already

8. Approach for Estimating Mercury Dry Deposition for AMNeT

(Presentation by Leiming Zhang)

- This presentation covered gaseous oxidized Hg (GOM), particulate-bound Hg (PBM), and gaseous elemental Hg (GEM)
- The Big Leaf model was used for estimating dry deposition of GOM; used 19 sites to get an estimated average annual Vd
- A size-resolved dry deposition model was used for estimating dry deposition of PBM; used assumed size distribution for fractions (PM2.5, PM2.5-10 and PM10)
- Coarse Hg contributed about 50-85% of the total particulate Hg dry deposition
- Vd for both fine and coarse fractions should be estimated
- The previous approach for estimating deposition of GEM used same model as for GOM but with different input parameters and with annual natural emissions from GRAHM
- The proposed new approach will use the Bi-directional Exchange Model

- Known GEM bi-directional exchange facts:
  1. Higher compensation points in light conditions
  2. Increased emissions with increasing soil temperature, pH, and moisture
  3. During springtime canopy growth the trend is toward deposition
  4. Increasing emissions with summer foliage
  5. Canopy wetness: Increased emissions in dry conditions and increased deposition when canopy and leaves are wet
  6. Higher atmospheric Hg concentrations lead to deposition, lower lead to emission
  7. Diurnal variations: emission in daytime/light conditions; deposition during nighttime/dark conditions
- Input data includes meteorology and land use data

Discussion:

- John Jantzen commented that there seems to be a very limited amount of coarse data available for actual concentrations and AMNet does not have PM coarse data (coarse Hg is referred to as PBM by Leiming). Dr. Jansen wanted to know how confident Leiming was about the elemental Hg deposition since the uncertainties are still substantial.
- Kristi asked for the caveats that go along with this work, and Leiming said that these have already been published
- Marty Risch said he has always struggles with the bi-directionality of elemental Hg and therefore started analyzing litterfall. There is evidence that elemental Hg is depositing in amount proportional to what is coming out of the atmosphere. GEM though is hard to get a handle on and it is the biggest part of Hg deposition. Marty said that it is important to point out that AMNet does not measure coarse Hg. There is also evidence that the landscape type that is modeled is very important as well
- John Jantzen commented that he doubts very much that ecosystem transport models have taken into account the coarse part and that the global budget balloon has many uncertainties
- Eladio asked whether elemental Hg methylates at the same rate as oxidized Hg? He also commented that we had only been reporting only about half of the Hg deposition that seems to be actually happening
- Donna commented that the compensation point is a function of gamma and that if gamma is not available then we have to develop this part. Her hope is that by the fall meeting details on how gamma is specified will be presented.
- In conclusion David asked Leiming to produce a white paper of how these estimates are made and the assumptions that are made

9. Nitrogen Flux Workshop Fall NADP Meeting 2013 Update

(Presentation by John Walker)

- A workshop inviting talks related to total N deposition was proposed to be held in conjunction with the 2013 Fall NADP meeting
- John has gotten very good response. Approximately 30 attendees from Europe, Asia and US/Canadian groups that do not typically attend NADP meeting
- Several workshop format scenarios presented

Scenario 1:

Integrate talks into regular NADP meeting. Friday would be organized as typical workshop with some overview talks and then breakout groups through late morning and early afternoon. Each breakout group would be tasked with a question/topic for which they will come back with recommendations to present to entire group. Although we would

end up with a ‘product’ this scenario is risky due to the need for good moderators to curtail discussions when necessary. Also, lots of prep, not enough time

Scenario 2:

Friday would be a series of many short presentations related to TDEP but with limited discussion time. The lack of discussion time with this scenario is a detractor and but would offer the advantage of consolidating TDEP related talks

Scenario 3:

Integrate most of the individual talks into regular NADP TDEP session as well as having a poster session. On Friday have series of 6-7 longer more informal talks lasting an hour or so. Talks could be a combination of invited talks on specific topics and from general submissions that directly address certain TDEP priorities

- For John the main goal of the workshop is to get the European groups’ perspectives plus deal with some of the issues that arose during the Madison TDEP meeting
- To this end it was suggested then to have invited speakers and then discussion centered around these talks
- Donna put forth whether we should have a panel discussion versus single talks
- The theme of the NADP symposium is “Going Back to the West”, but also meeting jointly during this Fall meeting with IMPROVE steering committee who has asked to present some issues. So on Thursday some Europeans can present to the whole symposium and then some of them on Friday. Will try to avoid having concurrent sessions
- Leiming suggested shortening the talks and to incorporate workshop format
- So in conclusion John is thinking three talks with panel format. Have yet to decide whether these should be “talks” or presented as questions to the panel?
- John to send an email out on format of workshop and then decide on final format based on response

10. Wrap-up

- Work on maps will continue and will be posted on CASTNET website in June
- David Gay, Eric Prestbo, David Schmeltz, and Marty Risch to work with Leiming on white paper
- Greg Weatherbee pointed out the TDEP name is not correct as we are really dealing with effective deposition and not total, i.e. not dealing with everything that hits ground
- Gary Lear looking for feedback on TDEP meetings. Leiming suggested shortening talks and having more discussion
- Thanks to all for attending!