

TDEP Committee Meeting, October 5, 2012, Portland, Maine

1. Welcome and Introductions

- Self introductions by all attendees (see attached attendance list)
- Motion to accept minutes from last committee meeting. Motion by Schwede and seconded by Krish

2. Hybrid Approach to Estimating Total Deposition Using CMAQ and Monitoring Data

(Presentation by Gary Lear) This presentation is on the TDEP web page:

<http://nadp.sws.uiuc.edu/committees/tdep/> Please refer to presentation for further information beyond what is provided in these minutes

- Why use a hybrid approach and why use CMAQ? An operational method was needed for estimating dry and total deposition; takes too long to wait for development of emission and meteorological profiles
- Actual measurements are likely more accurate at point of measurement than modeling but there are spatial and chemical gaps. Model was necessary to fill in the gaps and CMAQ is what is available
- Known Issues with this Approach:
 1. Error in both measurements and models
 2. NH₃: bi-di module not used in CMAQ v4.7, but available in CMAQ v 5.0
many uncertainties
lack of ambient measurements pre-2008
 3. Mass balance issues
 4. Spatial representativeness – ambient measurements are made where possible, not necessarily where needed
 5. Grid resolution – 36 km used currently; need to move to 12 km
 6. Deposition of unmeasured species held constant in this method
 7. Underestimation (by 10-50%) of deposition due to correlation of concentration and Vd
 8. Occult deposition – cloud and fog deposition not taken into account in this version
- Methodology:
 1. CMAQ CDC Phase runs were used; specifically 2002-2006 version (CMAQ v4.7) using 36 km grids and compared to 2007-2008 version (CMAQ v4.7.1) using 12 km grids
 2. All calculations were done as rasters
 3. Hourly mean, max, min and standard deviation calculated for deposition velocity (Vd) and flux for S and N species
 - 5 years of CMAQ runs
 - N=5 for each of 24-hours, 365 days
 - 36 km grids
 4. CMAQ runs aggregated to same timeframe as monitoring data (weekly for air concentrations)
 5. Weekly concentration grids were created using data from monitoring networks: CASTNET for HNO₃, SO₂, pNO₃, pNH₄, pSO₄
AMoN for NH₃ (2008 onwards)
Inverse distance weighting
12 km grids for concentrations
 6. Estimation of weekly dry deposition:

Concentration grids * CMAQ Vd = Deposition Product Grids

Vd applied from 36-km grids to corresponding cells in 12-km grids

7. Create weighting factor (Wf) grids for weekly deposition product (Wfp) and CMAQ (Wfc) grids
 - Sum of the weighting factors $Wfp + Wfc = 1.0$
 - Wfp ranges from 1.0 at the point of measurement to 0.0 at the maximum radius (Dmax) of influence, and decreases as the inverse distance squared $1/(Dmax-D)^2$
 - Dmax = 288km for all measurements except ammonia gas, which is 108km
 8. Merge weekly deposition products and CMAQ deposition as weighted averages of the two estimates
 - CMAQ used to fill in interstitial spaces ($Wfp=0$ and $Wfc=1$)
 9. Sum weekly dry depositions into annual time frame for all measured species
 10. Add CMAQ annual dry deposition of the unmeasured species (HONO, N2O5, NO, NO2, PAN, PANX, NTR) for total dry deposition
 11. Sum total dry deposition and PRISM-adjusted wet deposition from NADP/NTN for total deposition as 12-km grids
- Index of Variables Table: Summary of which network measures what variables and which variables are modeled
 - Results:
 1. Presentation of average deposition maps (2002-2006) for HNO3, pNH4, pNO3, Other N, Dry N, Total N, Dry S, and Total S
 2. Maps also presented for Average Percent of Total for Dry N and Wet N, Composition of Total N and S from 200-2010
 3. Mass Balance Bar Charts for N and S for 2002-2006 and for 2007-2008. Better agreement with 2007-2008 model run results for N. Total N results better than individual wet/dry results.
 4. Comparison of Hybrid Approach with CASTNET Results for Dry N, pNH4, HNO3 and pNO3 as well as for Dry and Total N Deposition with unmeasured species removed from hybrid approach
 - Results compare much better when unmeasured species removed from hybrid approach
 5. Addition of ammonia measurements in 2008 and beyond results in significant differences in N deposition (2007 versus 2010)
 6. Spatial Representativeness
 - Monitoring location not always spatially representative;
 - CMAQ probably does better job estimating gradients

Discussion: Lots of discussion was generated during the presentation and afterwards. The main points that arose from all the discussion were distilled into the categories of: 1) Changes to methodology for immediate application; 2) Caveats that should accompany this next revision; 3) Changes for the next version; 4) Subprojects; and 5) Products.

- **Immediate Changes to Methodology:**
 1. Investigation of 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
 4. Maintain 4-km gridding for wet deposition
 5. The CMAQ versions used will be cited
- **Changes for the Next Iteration:**
 1. Update with CMAQ 5.0

2. Use of the latest 5 years of runs: The 2004-2008 data set will replace the 2002-2006 data set
- **Caveats to be published with the Data**
 1. Incomplete characterization of the wet and dry organic N component resulting in an underestimate
 2. No bidirectional NH₃ in CMAQ model runs
 3. No lightning NO_x in CMAQ model runs
 4. No AMoN data available until 2008
 5. Underestimation of variation. Since deposition values are averages, more variation (than represented on the maps) could be expected with individual years
 6. Urban areas are not represented
 7. Spatial caveat
 - **Subprojects**
 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)
 - **Products**
 1. Total, dry and wet deposition maps for all components
 2. Map of inorganic N
 3. Web accessible – will be available on CASTNET site
 4. ESRI grid products
 5. Use for critical loads projects

3. Nitrogen Flux Measurement Workshop (John Walker)

- A workshop to be held in the US that focuses on state of the science and flux measurements
- European groups are further ahead of us in terms of flux measurements
- US groups are not well coordinated so the focus of this workshop would be to bring together groups that are making flux measurements
- Workshop would be held at the Fall 2013 NADP scientific symposium as a one day meeting with an option for workshop participants to present during a dedicated session of the symposium
- Plans to go ahead with the workshop approved by the group
- John, Bret, Leiming, Eladio and Berkeley will help organize and will get started by gauging the interest out there by the flux measurement community
- Bret would like to broaden scope to include some ambient concentration measurements for organic compounds
- This would most likely make it a two day conference which it may need to be in order to draw the Europeans

- However, this will also make it more difficult to schedule alongside the NADP conference

4. Total Nitrogen Deposition and Organic Nitrogen in Rocky Mountain National Park

(Presentation by Katherine Benedict) This presentation is on the TDEP web page:

<http://nadp.sws.uiuc.edu/committees/tdep/> Please refer to presentation for further information than provided in these minutes

- Total deposition determined by:
 - Wet Deposition – Daily/event bucket collection (NH₄, NO₃, ON)
 - Dry Deposition – 24- hour atmospheric concentrations (NH₃, HNO₃, PM_{2.5}, NH₄, and NO₃)
 - Vd from CASTNET
 - No gas phase ON
- Results from Rocky Mountain National Park (RMNP)
 - ON more abundant in aerosol PM_{2.5} than NO₃
 - Biomass burning important source of N in aerosol
- Grand Teton National Park (GTNP)
 - Increase observed in all measured N species with smoke
 - Other measured N-species (NO_x and NO_y) also increase with smoke
- Different types of N have different sources
- 404 different N-containing organic compounds were ID'ed in 36 samples
- Conclusions:
 - ON contributes 12-48% of total soluble N measured in aerosol
 - NH₄ was the dominant species in aerosol and precipitation
 - ON in wet deposition contributed similar fractions in RMNP and GTNP to total reactive N deposition
 - Still need to investigate structures of ON compounds; determine sources of ON, and make more measurements in more places

Discussion:

- Based on the statement that no single compound was identified in all the samples and given the over 400 different compounds that were identified, John thinks maybe the way to proceed is to focus on a class of compounds, prioritize and step through in a logical way
- Bret commented that the first thing to measure is the amount of total N in a bucket sample but also in the gas and particle phases. The speciation part is years in the making

5. A Path toward Routine Monitoring of Bulk Organic Nitrogen in U.S. Precipitation?

(Presentation by John Walker)

- Sources of ON are not well characterized.
- May be 10-20% of total N budget
- Most likely that ON biologically available to ecosystem
- Treatment of ON in chemical transport models for some of the compounds is lacking
 - Utilization of existing large-scale networks best way to get at this
- NADP and EPA study in 2009
 - Major conclusions are that about 40% of bulk ON is lost from standard NTN samples; ON is stable in lab if refrigerated
 - Samples should not be filtered
 - NO₂ is quantified to complete inorganic suite

- Real variability is evident across the 55 sites in the study
- Rapid loss of ON in samples is consistent with other studies but immediate refrigeration retards loss to only about 10%

PROPOSAL:

- Conduct 6 month study to verify the 10% loss estimate. Conduct study at BVL130 and Duke Forest. Look for site-specific differences.
- If 10% verified then start analyzing for TN and NO₂ at active AIRMoN sites for 1 year.
- Pursue participation from western sites
- After one year: bulk ON should be about 20% of total if little variability
- If highly variable, keep monitoring to identify where variability is coming from
- John wants to know if there is support for this proposal

Discussion:

- Tom Butler would be interested in participating as well as Bret
- Western sites a must
- Refrigerated bottom sample can facilitate some speciation; would be limited to sites with power
- Can do some investigation beforehand; look into Canadian methods
- Eladio would be interested in participating at SEARCH sites
- Can go to MDN style inlet with freezer at bottom to freeze in 20 minutes; shipping would be an issue
- Using preservative in NTN samples is a no go. Daily sampling way to go or a second sampler.
- Wayne: Include an intercomparison with total N analyzers. Shimadzu analyzer should be checked out to make sure that it is giving total N.
- Compare: AIRMon; AIRMon+refrigeration; AIRMon+thymol
Need a non-ag site and a high elevation site.
- Refrigeration of samples at BVL reduced NH₃ loss.
- Will go ahead with further study of stability in daily and weekly sampling.
- Bret interested in ON in snow pack. What did people think of that data?
 - Protocol is thought to be conducted via snow core sampling, then melted and then analyzed. Deposition value can be calculated from this as density of snow pack is measured.
 - Snow concentrations can be compared to winter NADP concentrations
 - Elevational difference gradients and investigations?

6. Wrap-up

Kristi: Thanks to Gary and Donna for map productions. The meeting was very productive. We will be sending out minutes and notes for review. Hope to see everyone in Madison for most likely a Monday meeting.

Gary: Thanks to all for participating.