

***Workshop on Atmospheric Deposition of Nitrogen***  
**Chesapeake Bay Program**  
**Science and Technical Advisory Committee**

**Held May 30, 2007 at the State University of New York, Binghamton, NY**

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Workshop summary and major findings:

Nutrient management in the Chesapeake region largely has focused on agricultural sources and on municipal wastewater treatment plants. This workshop was convened to advise the Chesapeake Bay Program on the role of atmospheric deposition as a source of nitrogen pollution to the Bay. The most recent evidence suggests that at least one third and probably significantly more of all the nitrogen that reaches Chesapeake Bay comes from atmospheric deposition, which also contributes to acid rain. Most of this deposition falls onto the landscape, and then a portion of it runs off and eventually reaches the Bay.

Much of the workshop focused on vehicle exhaust as a source of nitrogen. Reactive nitrogen gases are produced when fossil fuels are burned, and for the Chesapeake Bay region, vehicle exhaust is the single largest source of fossil-fuel derived nitrogen pollution. Until recently, scientists assumed that nitrogen pollution from vehicle exhaust behaved in the atmosphere in the same manner as pollution from electric power generating stations. However, evidence presented at the workshop suggests this is not true. Power plants release their pollution higher in the atmosphere, and the pollution is dispersed more widely and travels further than does the nitrogen from car exhaust. Most of the stations of the national network for monitoring acid rain – the National Atmospheric Deposition Program, or NADP -- are purposefully located far away from sources of pollution, as this system is designed to measure the regional imprint of acid rain and related pollutants. A disproportionately large amount of the nitrogen measured at the NADP sites appears to come from power plants rather than from vehicle exhaust. The pollution from vehicles is emitted very close to the ground, and according to the best available models, much of the nitrogen is deposited onto the ground within tens of kilometers. However, these models are not well validated, due to a lack of monitoring data on the dry deposition of nitrogen gases. Recent data presented at the workshop indicate that the rate of deposition of nitrogen in the immediate vicinity of roads and highways can be very high, with much of this occurring as the direct deposition of nitrogen gases to surfaces such as roads, trees, and buildings rather than falling in precipitation.

The workshop also considered agriculture as a source of nitrogen pollution to the atmosphere, particularly the volatilization of ammonia gas from animal wastes. Nationally, this has grown as a problem as more meat, poultry, and dairy products are

produced from large concentrated feedlot operations. For the Chesapeake Bay region, estimates from the CMAQ model suggest that 40% of the nitrogen deposition comes from this agricultural ammonia, and 60% comes from burning fossil fuels. The ammonia gas is even more reactive than most of the nitrogen gases from vehicle exhaust, and probably much of this ammonia is also deposited fairly close to the site of emission at the feedlots. As with the nitrogen from vehicles, most of the nitrogen volatilized from animal agriculture is not measured at the NADP monitoring sites.

Since much of the nitrogen pollution from vehicle exhaust and from animal agriculture is not measured at the NADP monitoring sites, the magnitude of these sources has not been appreciated in the past. Model results presented at the workshop indicate that the total amount of nitrogen deposited onto the watersheds of Chesapeake Bay is 40% greater than previously believed, when the deposition of nitrogen gases from these sources is included.

Reducing nitrogen pollution from vehicles is predicted to have a greater effect on reducing the pollution that reaches Chesapeake Bay than would a similar reduction in nitrogen emissions from power plants. This is true in part because much of the deposition of nitrogen from vehicle sources falls on impervious surfaces such as roads and parking lots, where little of the nitrogen is retained and most runs off downstream. In contrast, most of the nitrogen that is deposited onto forests is retained in the forest, and only a small portion moves downstream. Also, the proportion of deposited nitrogen that moves downstream increases dramatically as the overall rate of deposition increases, since soils, trees and other vegetation are limited in the amount of nitrogen they can retain. The hot spots of deposition near highways therefore are expected to lead to much greater runoff downstream to Chesapeake Bay. Urban and highways drainage systems aggravate this and accelerate the flux of nitrogen downstream. A key recommendation from the workshop is that there be much greater emphasis on treating urban and highway storm-water runoff to help reduce the nitrogen pollution that is deposited onto these surfaces. Diversion of runoff through created wetlands is one promising approach.

## Workshop conclusions and recommendations:

- What can lead to better management:
  - Modeling and fieldwork should be working together
  - Datasets of periods when monitoring is done would be helpful for modeling
  - Make datasets consisted and integrated
  - Instead of scattering resources in small field studies, use an integrated field campaign to obtain large field studies to feed models
    - Run five year strategic monitoring research
  - extensive low tech partnered with intensive high tech sampling
  - Obtain depositional velocities in areas of interest
  - BMPs for better management of atmospheric deposition of N
  - Build reliable NH<sub>3</sub> gas monitoring programs
  - Storm water management
    - Targeting areas near roads that receive deposition
    - What type of buffer strip to have?
      - Grassland or forest?
  - Spatial N component not being captured
    - N gas species (HONO, NO<sub>2</sub>, NO, NH<sub>3</sub>)
  - Better monitoring of N near roadways and other emission sources
  - Implement BMPs based on maximizing N retention based on three factors:
    - intrinsic retention ability
    - depositional velocity
    - concentration field
  - N in wet deposition can be up to 30% organic. Are we missing this measurement?
  - What mechanisms do we know for slowing the hydrograph response in urban centers? In rural agricultural landscapes?
  - Sub-grid cell modeling
    - Simple steps to lead to complex steps
      - taking CMAQ cells and comparing to other data to know if they suggest the same
      - Then CMAQ can be used for validating passive sampling devices to understand if they are worthwhile
  - Paired watershed study with vehicular traffic vs. clean
    - Do we get export?
    - How significant is vegetation and soil uptake?
  - Research to better estimate deposition velocities of N gases, particularly in urban areas, but also NH<sub>3</sub> in more rural areas.
  - Conduct research on NO, NO<sub>2</sub>, and NH<sub>3</sub> passive samplers in urban centers

Summaries of individual presentations at the workshop:

***Purpose and goals for the workshop***

Ron Entringer (New York State Department of Environmental Conservation)

The Chesapeake Bay Program estimates that air deposition accounts for 32 percent of the total nitrogen load to the Bay's tidal waters. However, this percentage could be higher since recent studies suggest that N deposition can be much greater near emission sources than away from these. If atmospheric deposition is responsible for more of the nitrogen load than previously estimated, management of air emissions would be significantly more beneficial. For example, to the extent emissions from vehicles are deposited locally, the resulting nitrogen flux is more difficult to account for in water quality monitoring. Do current models adequately consider this, and if not, how might they best be modified? Also, the importance of managing storm water and urban forests may be enhanced, since these may offer opportunities to control N export to the Bay.

It is also likely that management of agricultural emissions would be encouraged by better estimation and accounting of credits to effective practices. The extent and fate of atmospheric deposition on a local scale must be better understood to supplement the regional air and watershed models and to prepare for the model reevaluation that will allocate future loads. A key component of this assessment is the scale over which agricultural emissions of ammonia are deposited, and the extent to which this may give rise to hot spots of nitrogen saturation leading to disproportionate downstream flows of nitrogen.

The Goals for the workshop are:

- To determine if there is sufficient new science on atmospheric deposition of nitrogen to lead to better management of this nitrogen source, and if so, to summarize that science and its implications for better management. Based on the determination, the group will make recommendations.
- To highlight research needs that will lead to better serving management goals into the future.

For both goals, the focus is on deposition of nitrogen in relative close proximity to the site of emissions. This has been identified by the science community as an area that is likely underestimated and needs greater evaluation. It is important to note that controls on large stationary sources will result in a shift in proportions of sources, with emissions from agricultural and mobile sources becoming relatively more significant. If these sources are close to impervious surfaces, more of the deposited nitrogen enters water bodies, so emission controls have greater impact on nitrogen loads to the Bay.

### ***Introduction to emissions***

Wayne Robarge (North Carolina State University)

Understanding of emissions, reaction chemistry and depositional factors need to be improved so models predict deposition from animal agriculture more accurately. Emissions factors are annually, so there is a temporal disconnect with atmospheric models that run on a much finer time scale, such as the Community Multi-scale Air Quality (CMAQ) model.

The National Air Emissions Monitoring Study (NAEMS) is getting underway and will greatly improve estimates of ammonia emissions from animal agriculture, through intensive study of 14 sites nationwide. Measurements will include hydrogen sulfide, NH<sub>3</sub>, CO<sub>2</sub>, and temperature, measured 24 hours, 7 days per week. However, no data will be available publicly until at least 2010.

Nitrogen emissions from cropland may becoming more significant, due to increased corn production for ethanol, which requires more fertilizer use. Also, homeland security concerns are causing a shift in fertilizer use from ammonium-nitrate to UAN (Urea-Ammonium-Nitrate) solution and urea. In the rainy season, UAN can quickly decompose, increasing emissions. The extent to which deposited nitrogen (including ammonia, but also other species of N) re-volatilizes to the atmosphere as ammonia remains poorly known.

### ***Emissions to delivered load: Who does what to whom?***

John Sherwell (Maryland Department of Natural Resources), Mark Garrison (ERM), and Anand Yegnan (ERM).

The Power Plant Research Program has developed a source – receptor model to link sources of air emissions of reactive nitrogen [NO<sub>x</sub>, NH<sub>3</sub>] in an airshed to delivered nutrient-nitrogen [N] loads in a receiving water body. A model application has been derived for atmospherically derived N loads for the Chesapeake Bay. The modeling system uses the CALPUFF dispersion model to transport and transform emissions from the airshed and calculate a deposition load to the watershed. The airshed is a region encompassing approximately the states east of the Mississippi River and north from central Georgia to the Canadian boarder. The 1996 NET Inventory was used and included all sources divided into four categories: Electricity Generating Unit, Industrial [with identifiable stack], mobile [on-road] and area source for all other sources in the inventory. The meteorology used was the year-long MM4 simulation of 1996, which is close to the climatological average for the mid-Atlantic. The MM4 data are reprocessed through CALMET for input into CAPUFF. The model simulation is for one year with hourly time steps and outputs hourly deposition loading to a user defined receptor grid that in this instance covered the watershed. To translate the deposition load to a load delivered to the Bay, transmission factors for atmospheric deposition from the USGS

SPARROW model were applied. A source-receptor matrix is derived in which the relationship between each air emission source in the airshed can be linked to a modeled delivered load. Regional and temporal “what if” scenarios can then be analyzed with the matrix.

The results presented show the rank ordering of jurisdictions by emissions, deposition load and delivered load of oxidized nitrogen [NO<sub>3</sub><sup>-</sup>, HNO<sub>3</sub>]. The complexity of reduced nitrogen [NH<sub>3</sub>, NH<sub>4</sub><sup>+</sup>] modeling is discussed, particularly the poor quality of the emissions inventory and uncertainty in the deposition and evasion processes.

In addition to the regional scale modeling, a model application for near-field deposition is presented. Deposition loads adjacent to a section of I95 in Maryland were calculated. Direct dry deposition of NO<sub>x</sub> is shown to be high close to the highway. Nitrate deposition is relatively low along the highway as the chemistry that converts NO<sub>x</sub> to NO<sub>3</sub> does not occur to a significant extent in the short transport distances [ $<2\text{km}$ ] modeled. It is possible that conventional, Eulerian gridded models may not fully account for the high NO<sub>x</sub> deposition rates as model grids are usually significantly larger [ $>10\text{km}$ ] than the critical transport distance. This is an issue that needs additional investigation.

### ***Relationships between NO<sub>x</sub> Emissions and Wet and Dry Nitrogen Deposition***

Tom Butler (Institute of Ecosystem Studies IES Cornell University), Gene Likens (Institute of Ecosystem Studies), Francoise Vermeylen (Cornell University), and Barbara Stunder (NOAA Air Resources Lab)

NO<sub>x</sub> emissions in the Eastern USA have declined about 20% from 1997 to 2002, according to EPA estimates. These include reductions in both the Utility and Vehicle sectors which account for 25% and 54% of the total NO<sub>x</sub> emissions, respectively. This trend is also reflected in the airshed impacting the Chesapeake Bay watershed.

Total “measured” wet and dry N deposition (both oxidized and reduced), in the watershed is approximately 8.0 to 9.5 kg N/ha-yr and 60% of this is from wet and dry NO<sub>3</sub> deposition. Gaseous NH<sub>3</sub> and NO<sub>x</sub> deposition is not included in this estimate.

Using statistical random coefficient models we quantified the link between changing NO<sub>x</sub> emissions and their impact on measured wet and dry NO<sub>3</sub> deposition parameters (wet NO<sub>3</sub><sup>-</sup> concentration, and dry gaseous HNO<sub>3</sub> concentration). Our results, using data from 1991 to 2001, show that reducing NO<sub>x</sub> emissions reduces wet and dry NO<sub>3</sub> deposition with an efficiency of 70% to 90%. In other words, a 10% reduction in NO<sub>x</sub> emissions results in a 7 to 9% reduction in wet and dry NO<sub>3</sub> deposition, as measured by the NADP (wet) and CASTNet (dry) deposition monitoring networks.

The models were run using total NO<sub>x</sub> emissions and non-vehicle NO<sub>x</sub> emissions as the independent variables. The non-vehicle emissions models produced “better” results (eg. higher efficiencies and lower standard errors) than the total (vehicle + non-vehicle) emissions models. However both model forms were highly significant (P-value for the

regression slopes  $<0.0001$ ). The non-vehicle emissions data are considered more accurate than the vehicle NO<sub>x</sub> emissions data. In addition the wet (NADP) and dry (CASTNet) sites are “regionally representative” and may not reflect more local N deposition from vehicles that may occur near roadsides.

***Deposition of NO<sub>2</sub> and NH<sub>3</sub> gases near roads and the relationship to vehicle emissions***

Roxanne Marino (Cornell University), Bob Howarth (Cornell University), Neil Bettez (Cornell University), and Eric Davidson (Woods Hole Research Center).

We have measured near-source dry deposition of nitrogen gases (NO<sub>x</sub>, NH<sub>3</sub>) from vehicle emissions on Cape Cod, MA. Recent evidence suggests that total nitrogen deposition in urban and suburban areas can be substantially higher than estimated using data from national monitoring stations, which are located purposefully away from such areas, and which do not measure dry deposition of some important gaseous components. We examined summertime patterns of nitrogen pollution and deposition along 5 to 150 meter gradients away from two roads (16,000 vehicles per day average), using gas concentration measurements made with passive samplers and literature-based depositional velocities, and measurements of nitrogen in bulk (open field) and throughfall collectors. Bulk nitrogen deposition shows no pattern along the gradient, whereas throughfall nitrogen is greater than bulk, and is highest nearest the road and decreases with distance. Gaseous nitrogen deposition is highest near the road edge and falls exponentially with distance, decreasing 60 to 80% over 20 meters. We estimate that within 50 to 100 meters of the roadway edge and in average to wet years, dry gaseous nitrogen deposition is half of the total nitrogen deposition, with two thirds from NH<sub>3</sub>, and one third from oxidized nitrogen. In dry years, the proportion of total nitrogen deposition from dry gaseous nitrogen species is likely greater, increasing total nitrogen deposition estimates from bulk precipitation measurements by 100% or more. Our results indicate that vehicle traffic is likely a significant source of nitrogen deposition to developed coastal areas.

***Refinements to the Daily Ammonium and Nitrate Wet-Fall Concentration Models for the Chesapeake Bay Watershed***

Jeffrey Grimm (Cyclometrics Environmental Consulting)

Refinements to the daily NH<sub>4</sub> ion and NO<sub>3</sub> ion wet-fall concentration models of CBW include more NADP/NTN precipitation chemistry stations representing a wider range of deposition environments, particularly agricultural settings (39 sites vs. 29 sites); longer sample history (1984 through 2005 vs. 1984 through 2001); improved representation of land cover and land use activities; improved delineation of ammonia and nitrous oxide emissions; and, quantification of emissions levels and impacts through emissions transport modeling and storm trajectory analyses. We documented emission sources associated with different land use covers for the watershed, included cropland, livestock production areas, industry, transportation corridors, and forest. This generated

geographic distribution of NH<sub>3</sub> emissions and nitric oxide emissions associated with agricultural and other point sources.

The revised ammonium wet-fall concentration model shows deposition from 1984-2005 was generally high in spring, and tapers off in summer and into the fall. Model outputs show elevated NH<sub>4</sub> deposition closer to the Bay and less NH<sub>4</sub> deposition in upstate areas. Deposition of NH<sub>4</sub> was shown to increase over 60 % (> 1 kg/ha) near the Bay. The model for NO<sub>3</sub> wet fall deposition shows some similar patterns to NH<sub>4</sub>. Before 2000, the heaviest deposition occurs in northern part of the watershed, because most comes from the Ohio Valley. Although NO<sub>3</sub> deposition has been decreasing slightly near the Bay, in the northern and western parts of the watershed, it is decreased over 40 % (> 2 kg/ha).

***Inorganic nitrogen retention and export in forested watersheds in the upper Susquehanna River basin***

Christine Goodale (Cornell University)

Atmospheric deposition contributes a large fraction of the annual nitrogen (N) input to the basin of the Susquehanna River, a river that provides two-thirds of the annual N load to the Chesapeake Bay. Yet, there are few measurements of the retention of atmospheric N in the Upper Susquehanna's forested headwaters. We characterized the amount, form (nitrate, NH<sub>4</sub><sup>+</sup>, and dissolved organic nitrogen), isotopic composition (δ<sup>15</sup>N- and δ<sup>18</sup>O-nitrate), and seasonality of stream N over two years for 8-15 catchments. We expected high rates of N retention and seasonal nitrate patterns typical of other seasonally snow-covered catchments dormant season maxima and growing season minima. Coarse estimates of N export indicated high rates of inorganic N retention (> ~90%). Streams had unexpected seasonal NO<sub>3</sub><sup>-</sup> patterns with summer peaks (0.2-1.3 mg N/l), October crashes (<0.01 mg N/l), and modest rebounds during the dormant season (<0.01-0.17 mg N/l). Stream δ<sup>18</sup>O-nitrate values indicated microbial nitrification as the primary source of stream nitrate, although snowmelt or other atmospheric source contributed up to 47% of stream nitrate in some March samples. The autumn nitrate crash coincided with leaf-fall, likely due to in-stream heterotrophic uptake of N. Hypothesized sources of the summer nitrate peaks include: delayed release of NO<sub>3</sub><sup>-</sup> previously flushed to groundwater, weathering of geologic N, and summer increases in net nitrate production.

***Predictions from SPARROW model on retention, and possible inferences for near-source deposition of nitrogen in urban and suburban areas***

Richard Alexander (USGS)

USGS has modeled the fate of atmospheric N deposition in watersheds using SPARROW (Spatially Referenced Regressions on Watershed Attributes) to predict fluxes and concentrations in streams, especially in those which are not monitored. We track the origin and fate of contaminants from upstream to downstream.



The SPARROW model works with large scale geographical information, such as precipitation, land use, soils, stream and reservoir water velocity. Land and water processes are separated in this mass balance model. SPARROW incorporates urban sources, atmospheric deposition, farm fertilizer, N<sub>2</sub> fixation, pasture/rangeland (non-recoverable animal manure), background and residual sources (lands in forest, barren, shrub). Land to water delivery is based upon climate, soils, topography, and artificial drainage. It also considers aquatic systems such as streams and reservoirs, but does not deal with much atmospheric N deposition, but can be improved using CHIRP. SPARROW does not explicitly deal with NH<sub>3</sub> because of uncertainty with the source receptor relationship, possibly resulting from co-linearity with animal populations. Research needs include improved quantification of terrestrial sources of atmospheric N deposition such as vehicle emissions and NH<sub>3</sub> emissions, and continued improvements in model inputs and riverine outputs.

### *Understanding atmospheric NO<sub>3</sub> sources to landscapes and implications using stable isotopes*

Emily Elliott (University of Pittsburgh)

We work to characterize N isotopes from deposition to see if we can distinguish electrical utilities vs. cars and natural sources. Different NO<sub>x</sub> sources have different isotopic signatures. Natural sources have low <sup>15</sup>N values, whereas, fossil fuel combustion have high <sup>15</sup>N values. A new method is being used for isotope studies that use denitrifying bacteria to reduce NO<sub>3</sub> to N<sub>2</sub>O gas.

We looked at NADP data from sites in the US. In the Northeast, data display higher <sup>15</sup>N absolute values and greater seasonal ranges in winter than summer. We can explain about 80% of variability of NO<sub>x</sub> emissions, because <sup>15</sup>N is a great tracer of stationary source NO<sub>x</sub>. No correlation between <sup>15</sup>N and vehicle NO<sub>x</sub> emissions is evident, because NADP sites are away from roads. Local deposition near roadway environments is mostly deposited as dry NO<sub>2</sub> rather than wet NO<sub>3</sub>, which is collected by NADP. NO<sub>2</sub> concentrations decrease by 90% when away from road. NO<sub>x</sub> emissions from vehicles are available for plant uptake. In pine needles and tree rings, total <sup>15</sup>N values are greater near roads than away from roads with higher <sup>15</sup>N values closer to the roads in mosses. Up to 200 mg L<sup>-1</sup> of NO<sub>3</sub> is detected in ground seepage water at the road edge. Hydrologic alterations in road areas may accelerate delivery of atmospheric nitrate to surface waters. <sup>15</sup>N can be a useful tool for distinguishing sources in various N forms.