

Atmospheric ammonia measurements at low concentration sites in the northeastern USA: implications for nitrogen deposition and comparison with CMAQ estimates

Tom Butler^{*1,2}, Roxanne Marino², Donna Schwede³, Robert Howarth², Jed Sparks² & Kim Sparks²

Long-term monitoring sites for atmospheric deposition have only recently begun to measure NH₃ gas. We evaluate the importance of ammonia deposition at two headwater areas of the Susquehanna River, that are remote from major sources of ammonia emissions: Connecticut Hill (CTH) in central NY State and the Kane Experimental Forest (KEF) in NW Pennsylvania.

We used Ogawa passive samplers to measure ammonia concentrations during all seasons over several years for CTH, and mainly in 2009 for KEF. Chamber calibration studies and field comparisons with annular denuders for ammonia validated the use of these passive samplers over a range of temperatures and humidities observed in the field. Seasonal NH₃ concentration trends were consistent for these, and another forested site near CTH. The annual mean concentrations were twice as high at CTH than at KEF: 0.48 vs 0.24 $\mu\text{g NH}_3 \text{ m}^{-3}$. For CTH, this value is very close to the estimate from the CMAQ model, while at KEF the mean of our measured values was 2.5-fold higher than the CMAQ estimate.

Concentration and deposition velocity (V_d) can be correlated and ignoring this correlation when using average values to determine flux can result in errors. Monthly *concentration-weighted* V_d 's, based on hourly CMAQ concentrations and hourly V_d 's, and applied to mean monthly CMAQ concentrations, produce nearly the same depositions based on the sum of hourly depositions, thus compensating for the correlation effect. Using our ammonia concentration data and these monthly concentration-weighted V_d 's, we estimate dry gaseous NH₃ deposition as 2.0 and 1.4 kg N ha⁻¹ yr⁻¹ at CTH and KEF, respectively. Approximately 70% of this deposition occurs between April and September.

CTH and KEF CMAQ estimates of all modeled N deposition species are compared with total deposition estimates incorporating CASTNET, NADP and passive sampler data, where available (hybrid approach). CMAQ and the hybrid approach yield deposition values of 9.7 and 9.5, respectively for CTH, and 10.1 and 9.2 kg N/ha-yr, respectively for KEF. Approximately 85% of these depositions are from dry HNO₃ and NH₃, and wet NO₃⁻ and NH₄⁺. The hybrid approach, based on measured concentrations, yields lower depositions for HNO₃ and higher NH₃ depositions. Wet NH₄⁺ deposition is 20% to 25% higher than CMAQ estimates, and wet NO₃⁻ are nearly equal for both approaches. CMAQ estimates of wet organic N deposition for these sites, appear to be too low by ~0.5 to 1.0 kg N/ha-yr, compared to literature values.

*corresponding author (tjb2@cornell.edu ; 607 255-3580); ¹Cary Institute of Ecosystem Studies, Millbrook, NY; ²Ecology & Evolutionary Biology, Cornell University, Ithaca, NY; ³Atmospheric Modeling and Analysis Division, National Exposure Research Lab, US EPA, RTP, NC