Measuring Exchange of Ammonia Over Cropping Systems with the Modified Bowen Ratio Technique

Paul V. Doskey[1], David R. Cook[2], and Michael E. Caughey[3]

[1]Department of Civil and Environmental Engineering and School of Forest Resources and Environmental Science, Michigan Technological University.

[2]Environmental Science Division, Argonne National Laboratory.

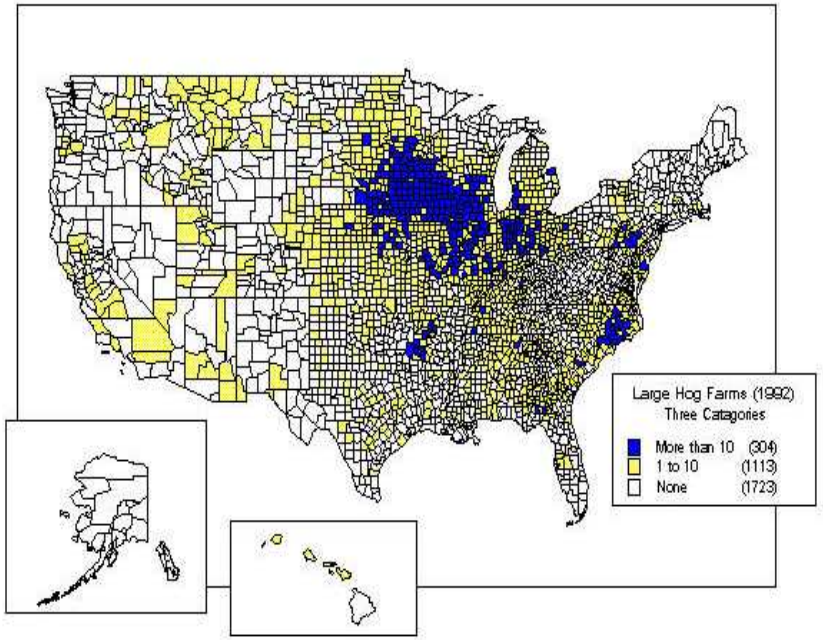
[3]Center for Atmospheric Science, Illinois State Water Survey.

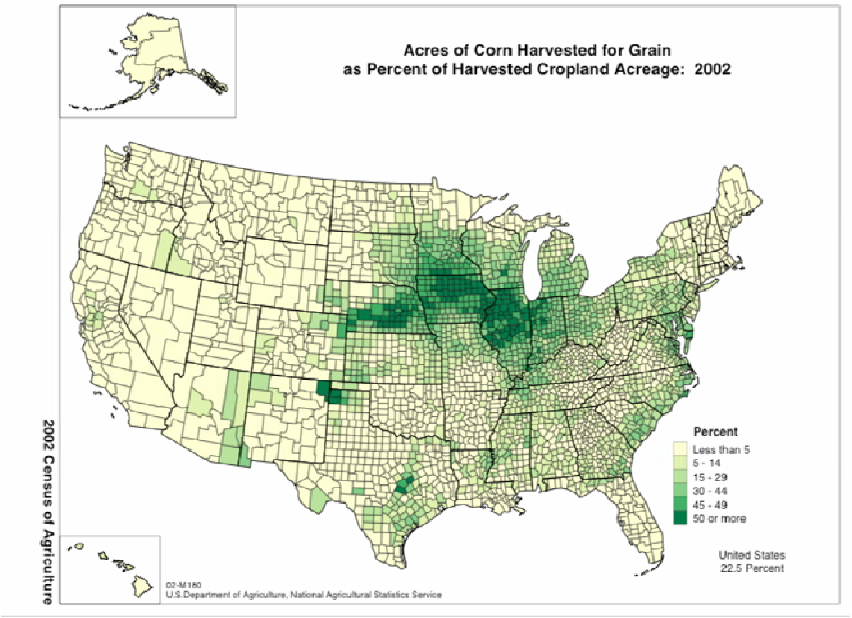
Presentation Outline

- Ammonia in the Midwest.
- Research goals and objectives.
- Features of the modified Bowen ratio technique for measuring exchange of ammonia over cropping systems.
- Research strategies to improve understanding of the fate and transport of emissions from Midwest agroecosystems.

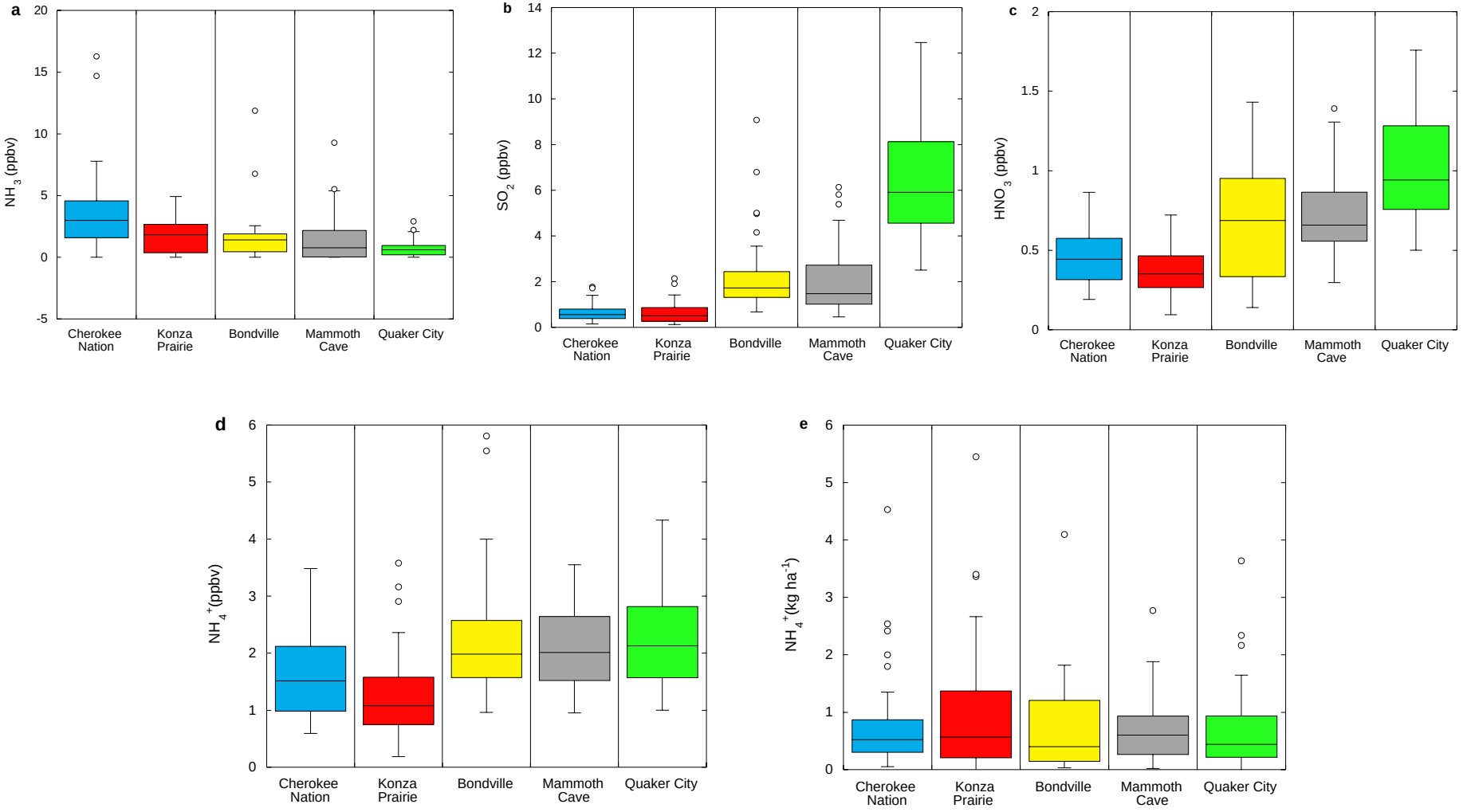
Ammonia in the Midwest

- Ammonia (NH_3), the only gas-phase alkaline substance in the atmosphere, reacts rapidly with sulfuric and nitric acids generated primarily by fossil fuel combustion to produce haze-forming fine aerosol.
- The principal sources of atmospheric NH_3 are animal waste, nitrogen fertilizers, decomposing plant material, biomass burning, and fossil fuel combustion.





Midwest CASTNET and NADP Data

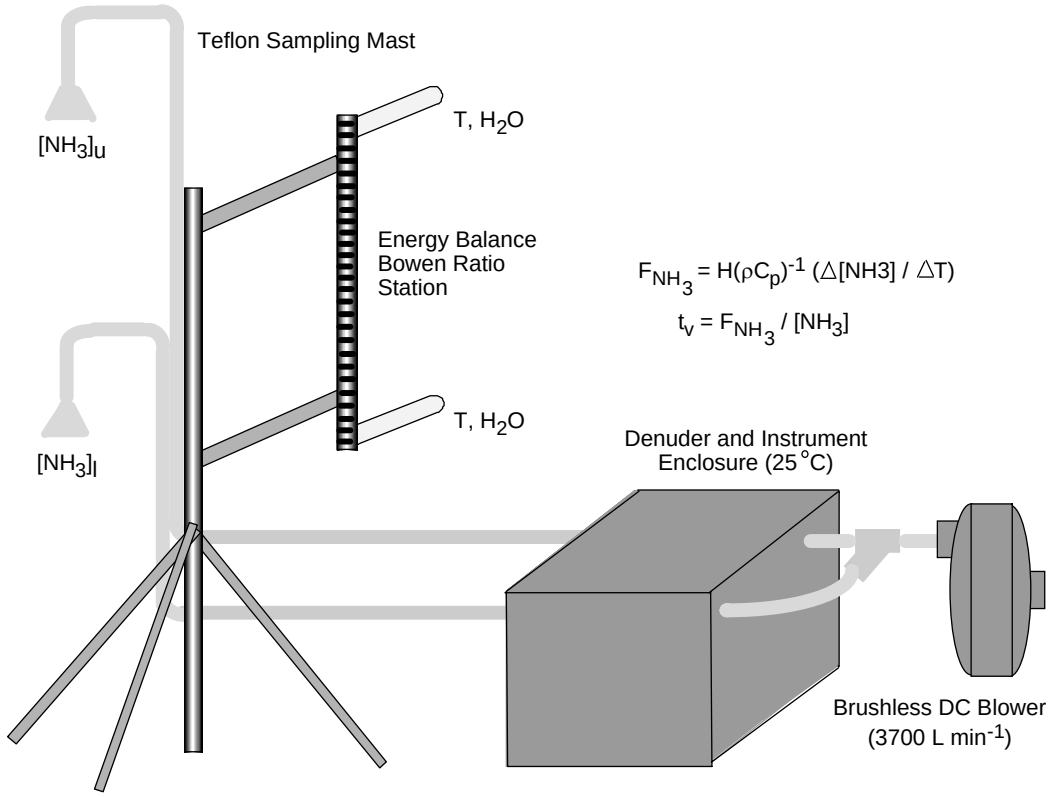


Research Goals and Objectives

- Improve understanding of plant physiological and environmental factors that affect the exchange of NH_3 with agricultural crops.
- Perform a field investigation of the exchange of NH_3 with corn and soybeans.
- Develop a parameterization for bi-directional exchange of NH_3 for the Argonne Dry Deposition Module.
- Assess the transformation of NH_3 emissions in the rural PBL by coupling the Argonne Dry Deposition Module with a one-dimensional (1-D) model of the chemistry and dynamics of the rural PBL.

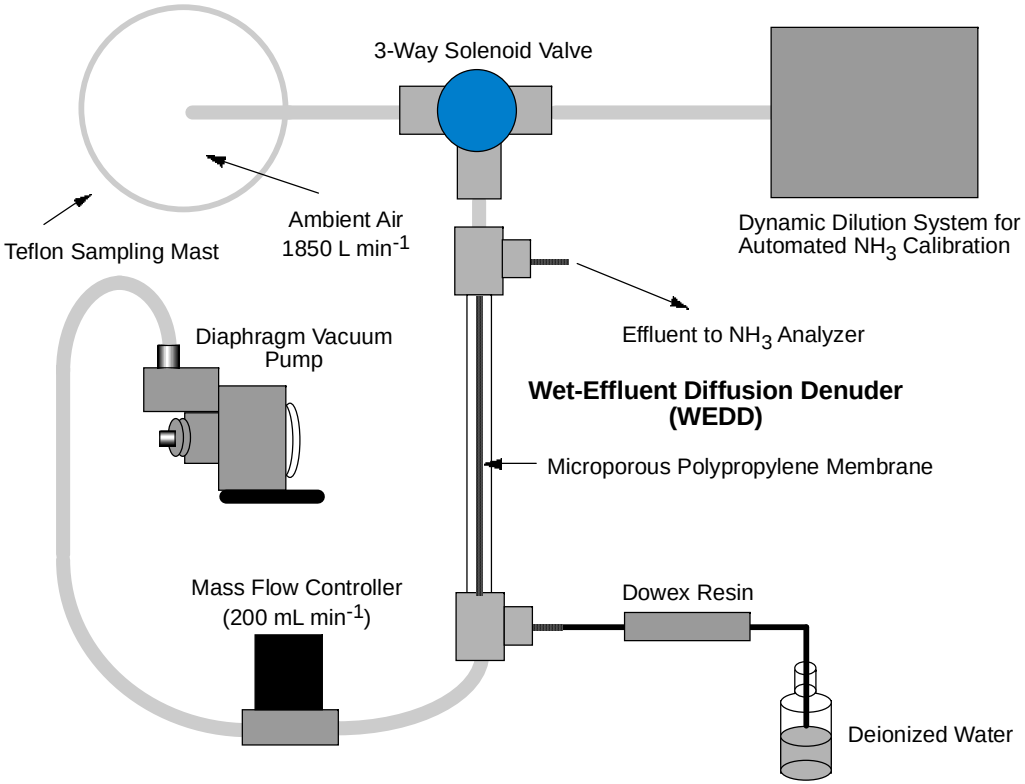
Measurement Approach

- Semi-continuous measurements of the gradient in NH_3 concentrations made in concert with continuous measurements of the gradients in water vapor density and air temperature.
- High-throughput flow of ambient air from 2 elevations above the surface through Teflon® PFA sampling masts to NH_3 sensors.
- NH_3 sampling and analytic systems located in temperature-controlled enclosure.



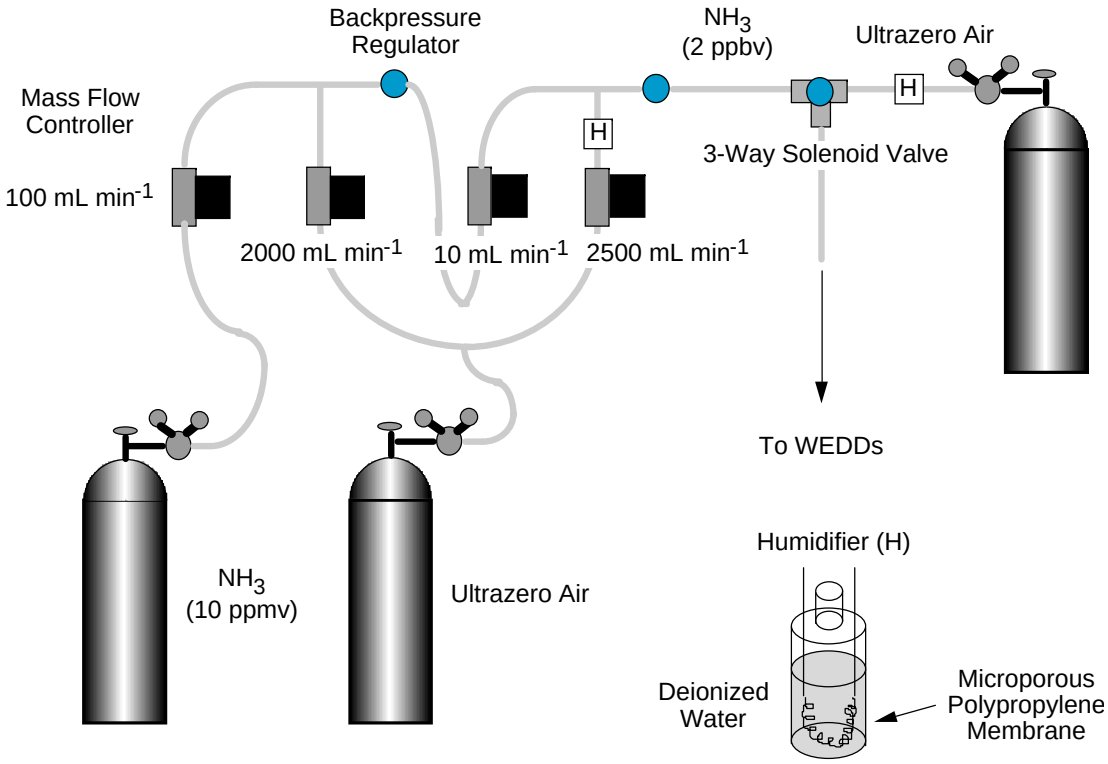
Wet-Effluent Diffusion Denuder

- Outer jacket of the WEDD is constructed with 3.9-mm-i.d. Pyrex glass tubing and a 3.2-mm-i.d. PTFE inner sleeve.
- A 3-way solenoid valve (Teflon® PFA, PTFE) directs ambient air from the sampling mast or calibration standard to the WEDD.
- Gas-phase NH_3 diffuses from the sampled air stream through a microporous PPE membrane and is collected in deionized H_2O.



Automated Calibration System

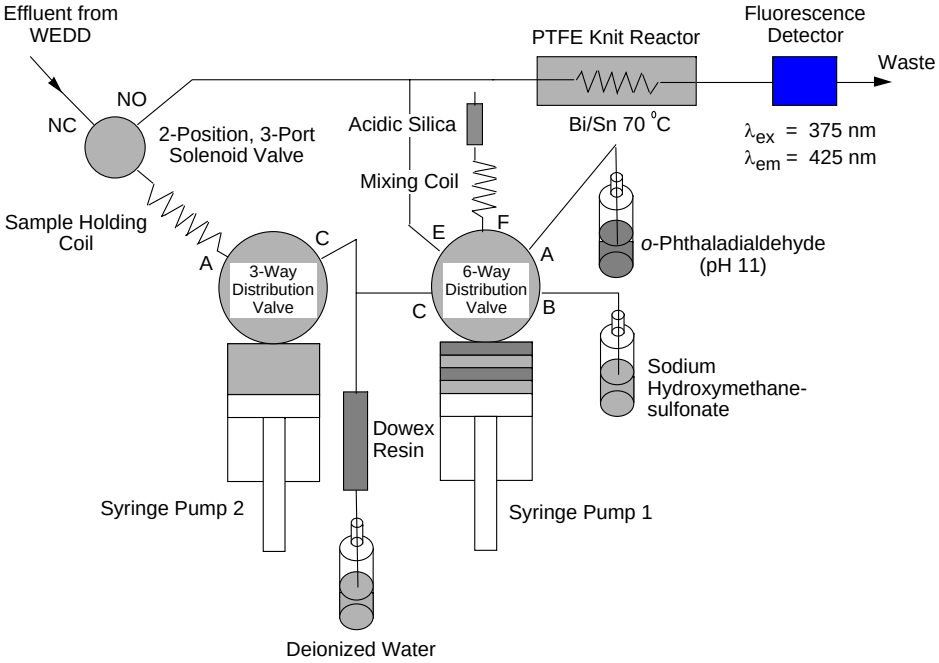
- A 3-way solenoid valve (Teflon® PFA, PTFE) is used to select a dilute humidified NH_3 gas standard or humidified ultrazero air.
- A series of mass flow controllers dynamically dilutes a 10-ppmv NH_3 gas standard to 2 ppbv. The final dilution is performed with humidified ultra zero air.



Hybrid Fluorometric Flow Analyzer

- NH_3 is measured by flow injection analysis of 1-sulfonatoisoindole, a fluorescent compound produced by the reaction of NH_3 with *o*-phthaldialdehyde (OPA) and sulfite at pH 11.
- The OPA-sulfite-NH_3 reaction occurs at 70° C in a PTFE knit reactor.
- Fluorescence is measured at 425 nm by an LED photodiode-based detector.

(Amornthammarong et al., *Anal. Chem., 78*, 1890-1896, 2006.)



Measurement Protocol

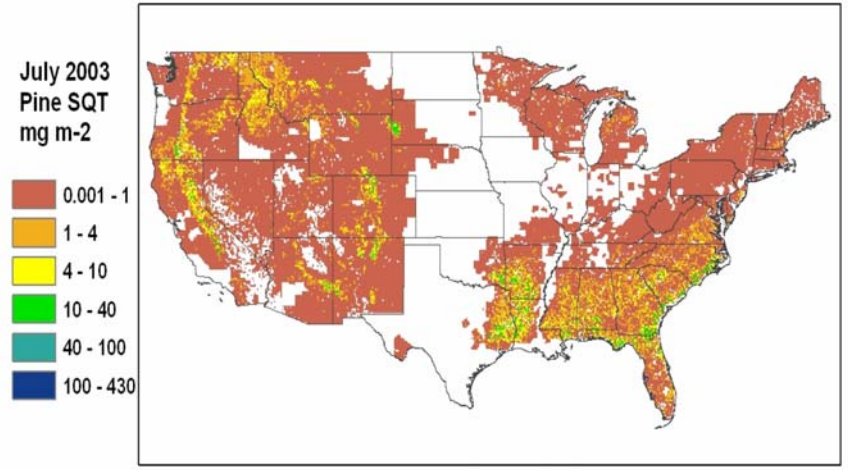
- Two measurements of the NH_3 gradient before T and H_2O sensors are exchanged.
- Periodic one-point calibration at 2 ppbv.
- Periodic zero determination to evaluate denuder memory effects.
- Twice monthly cleaning of the denuder with methanol.
- Twice monthly, five-point calibration by manual injection of aqueous NH_3 standards when solutions are replenished.
- Twice monthly evaluation of Teflon® sampling mast integrity.

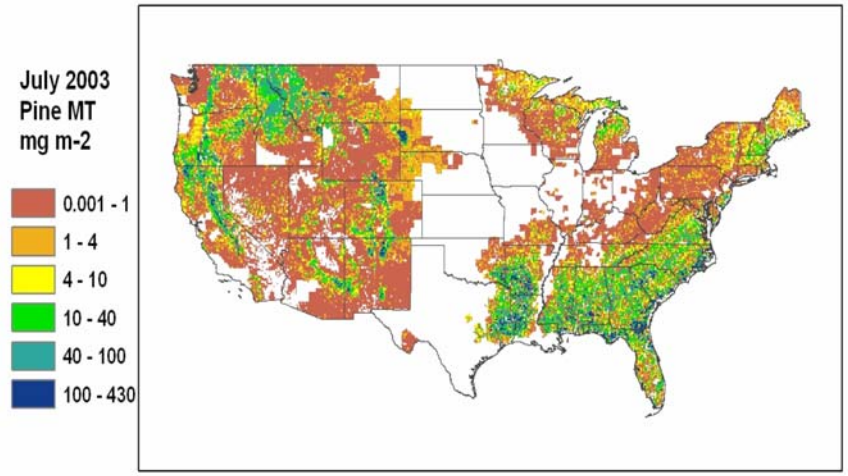
Research Strategy to Evaluate the Impact of Agricultural Emissions on Midwest Regional Air Quality

- Augment air monitoring sites in source regions with high-frequency measurement capabilities for gas- and aerosol-phase chemical species.
- Conduct multi-agency field campaign to make regional measurements of air chemistry at the surface and aloft.

Emissions of Biogenic SOA Precursors From The Ozarks

The Ozarks region is a rich source of isoprene, monoterpenes, and sesquiterpenes.

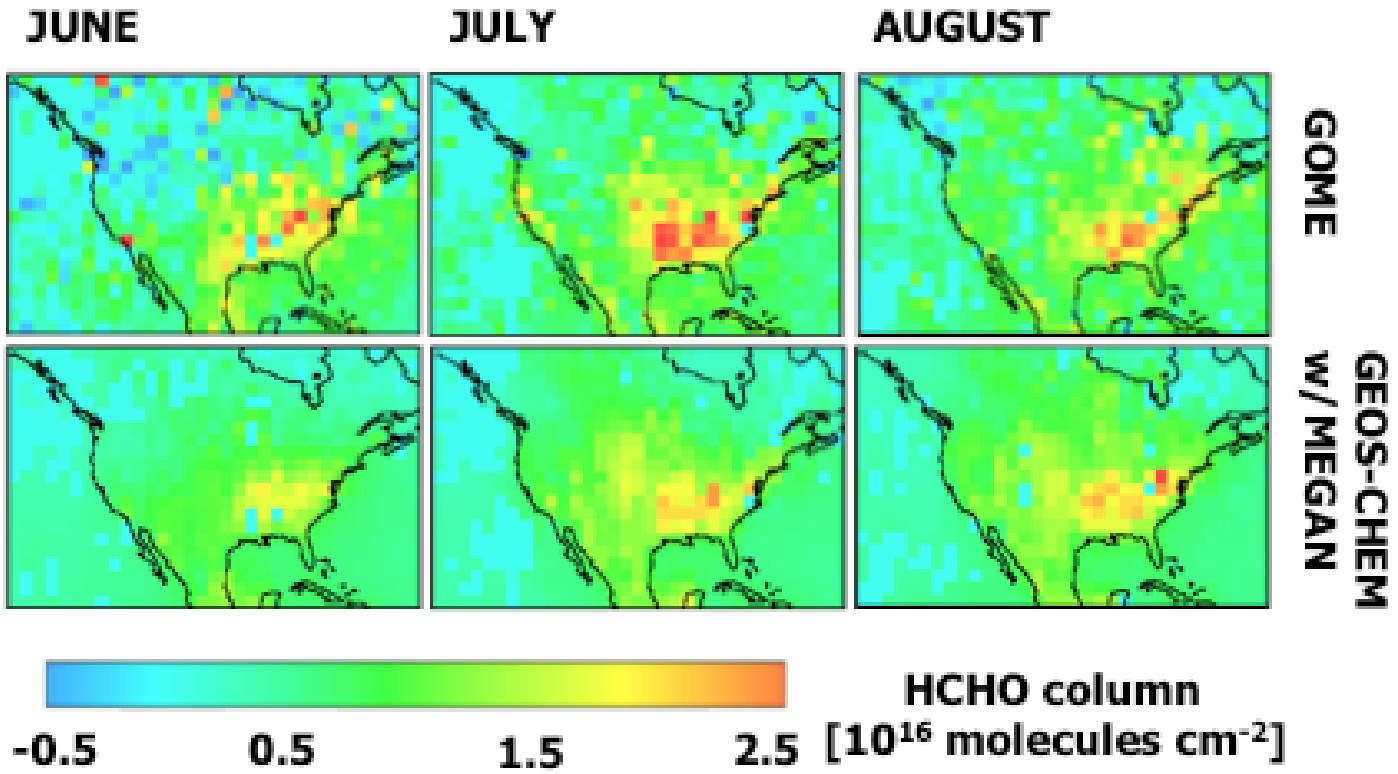




(Guenther et al., *Atmos. Chem. Phys.*, *6*, 3181-3210, 2006.)

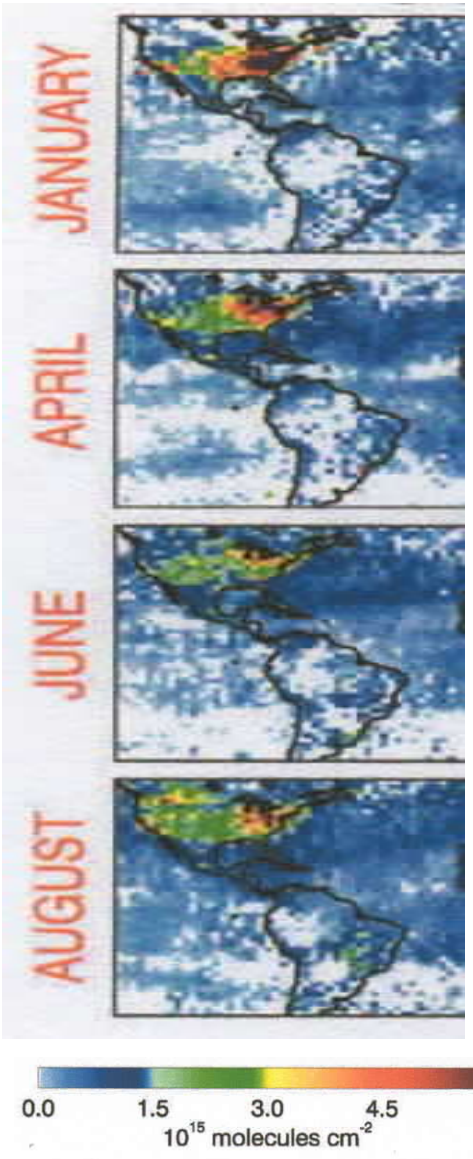
A Region of High Photochemical Activity

Monthly Mean Column HCHO Over
North America

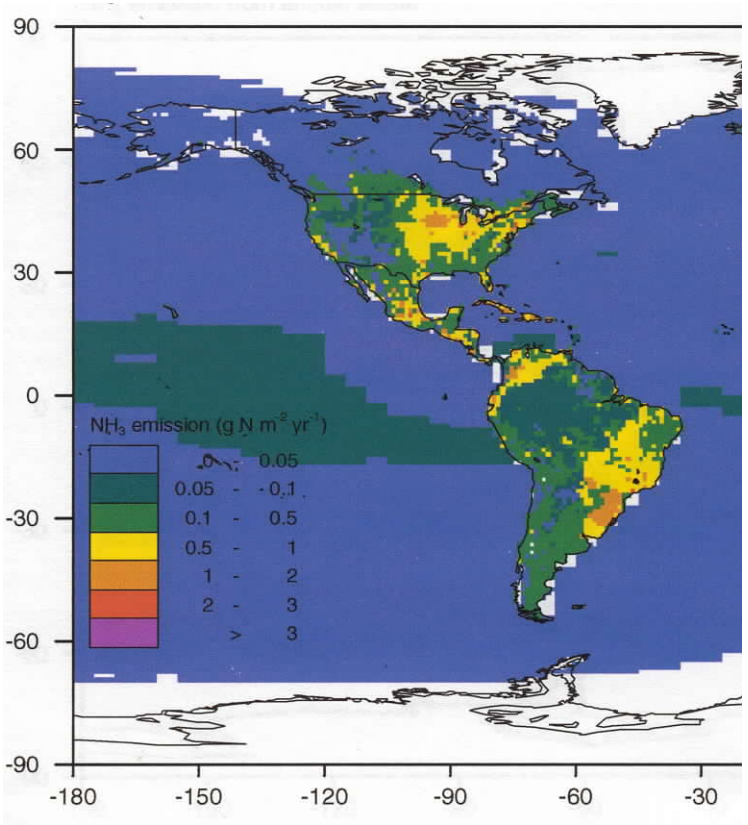


(Guenther et al., *Atmos. Chem. Phys*., *6*, 3181-3210, 2006.)

Emissions of SIA Precursors from Agricultural Soils



GOME observations of column NO_2

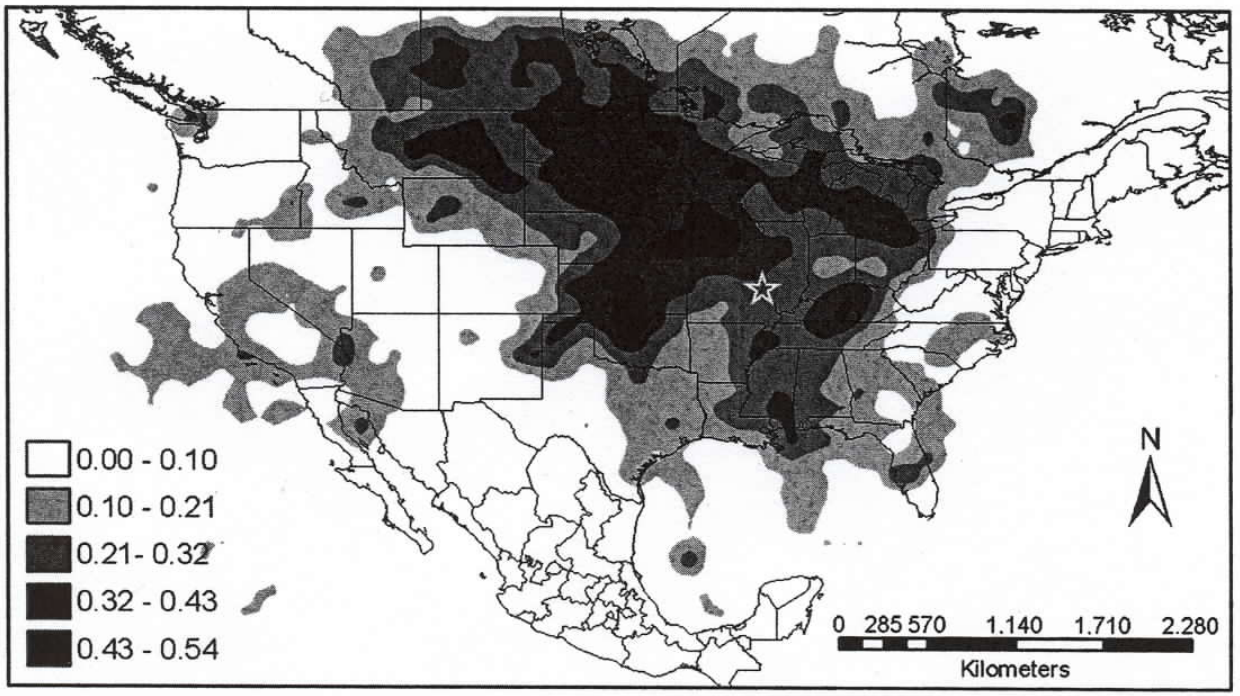


Estimated NH_3 emissions from all sources.

- Satellite observations indicate soil-derived NO_x might be 70% greater than earlier predictions (Jaeglé et al., *Faraday Discuss., 130*, 407-423, 2005).
- Animal waste is the largest source of NH_3 followed by fertilized agricultural fields (Asman et al., *New Phytol., 139*, 27-48, 1998).

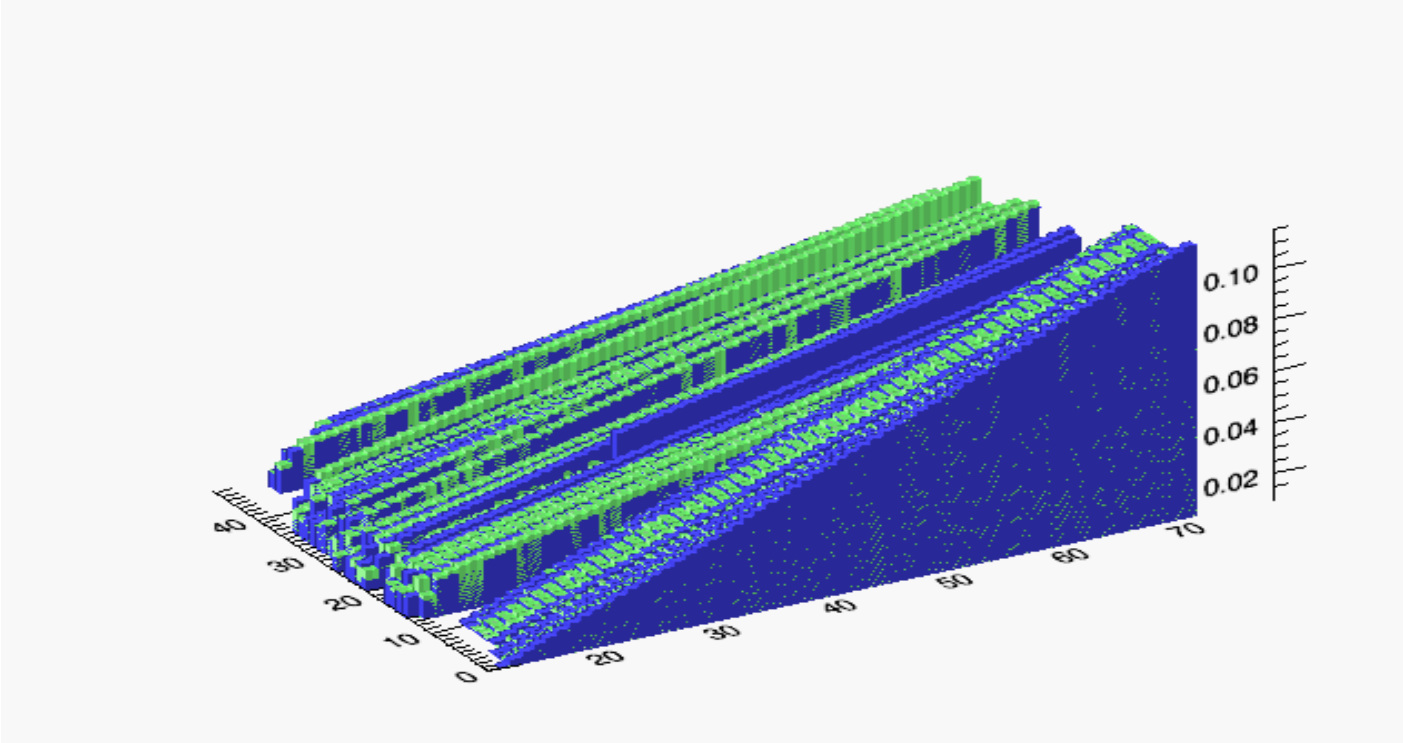
Nitrate Aerosol and the Midwest Cornbelt

Potential Source Contribution Function for NO_3^-



- The contribution of regional ammonium nitrate to fine aerosol in St. Louis, MO was estimated to be 63% (Lee, J.H. & Hopke, P.K., *Atmos. Environ., 40*, S360-S377, 2006).

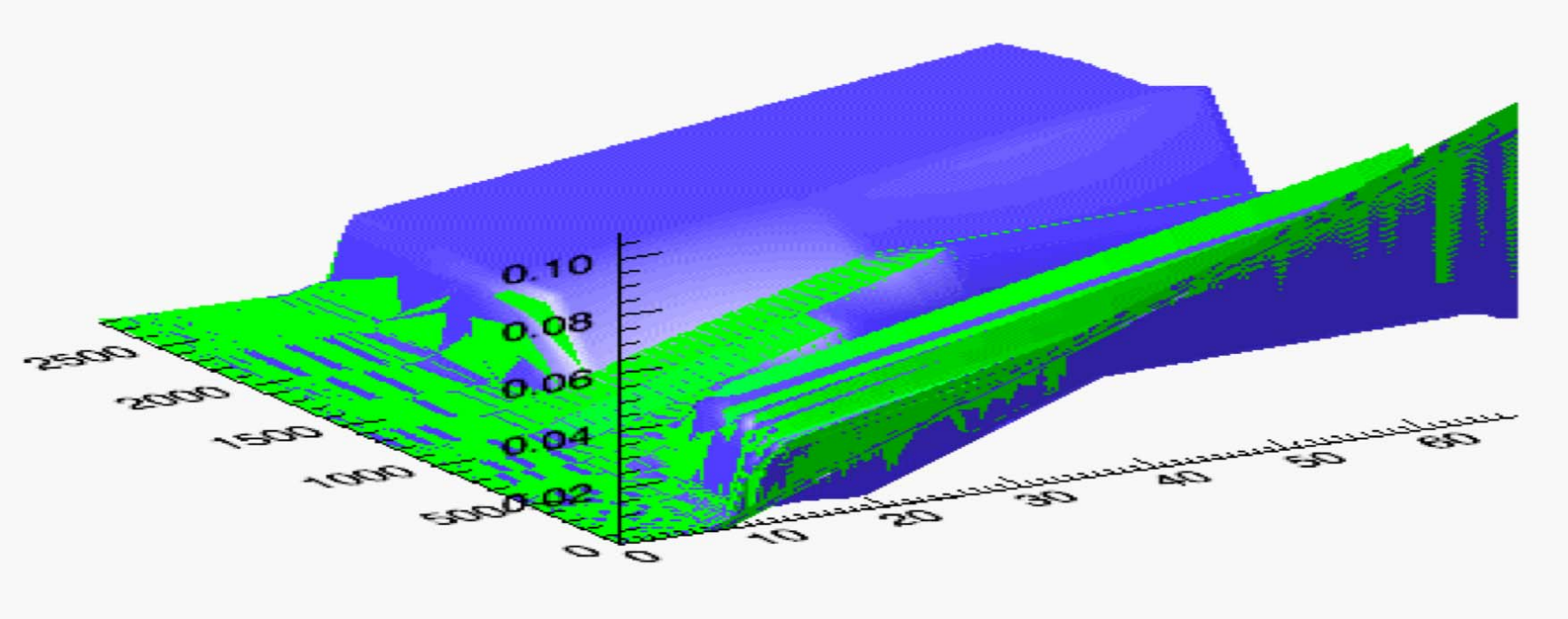
Aerosol SO_4^{-2} as a Function of NH_3, Time, and Elevation in the PBL



- X-axis, time (hr) from start of model simulation.
- Y-axis, altitude (grid 40 = 3 km).
- Z-axis, aerosol SO_4^{-2} at 1 ppbv NH_3 (blue) and 5 ppbv NH_3 (green).

- At higher altitudes there is more SO_4^{-2} aerosol formed at higher NH_3 mixing ratios than at low NH_3 mixing ratios, which suggests NH_3 might limit aerosol production in the rural PBL at certain elevations and times.

Aerosol SO_4^{-2} and NO_3^- as a Function of Time and Elevation in the PBL

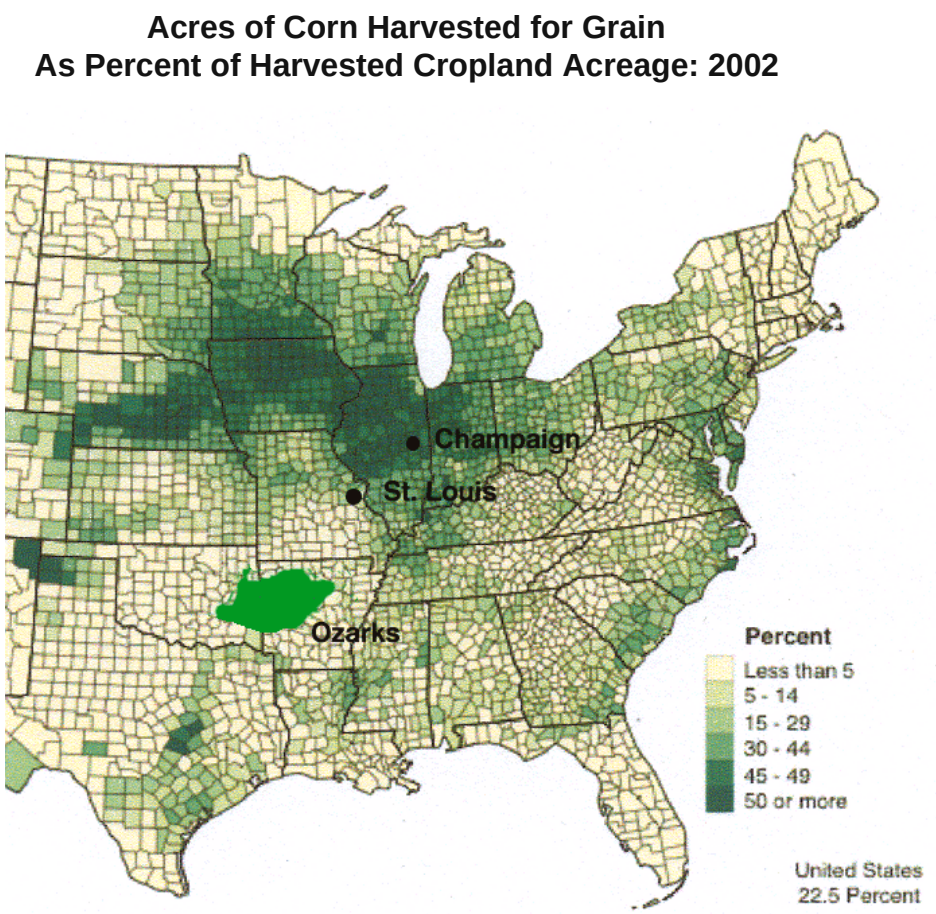


- Aerosol SO_4^{-2} (green) forms more rapidly than NO_3^- at all elevations of the PBL.
- Aerosol NO_3^- (blue) is formed at higher elevations of the PBL.

Geographic Domain of the Midwest Aerosol Production Experiment (MAPEx)

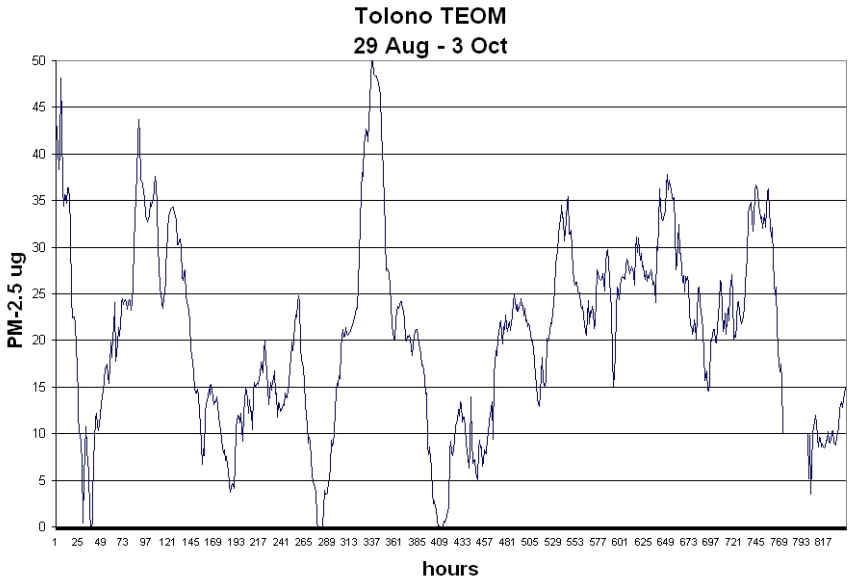
Surface Sites

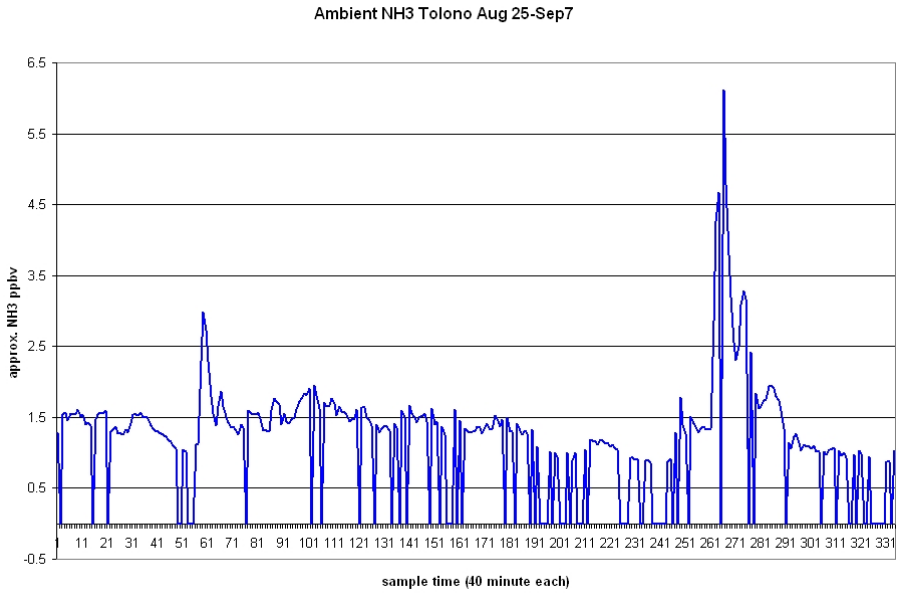
- St. Louis, MO - USEPA Midwest Supersite
- Champaign, IL - ISWS Bondville Environmental and Atmospheric Research Site (BEARS)
- Savoy, IL - NH_3 flux measurements



Create Air Monitoring Sites in Source Regions

- High-frequency monitoring of trace gas and aerosol species that are key reactants and products in the NH_3-HNO_3-H_2SO_4-H_2O system of inorganic aerosol production (e.g., NO, NO_2, HNO_3, O_3, VOCs, SO_2, NH_3, NH_4NO_3, $(NH_4)_2SO_4$).





- A TEOM trace of a continuous $PM_{2.5}$ mass measurement.

- A direct sampling gas/particle ion chromatogram of NH_3 (40 min sampling frequency).

Conclusions

- A relatively inexpensive but robust sampling and analytic technique is being developed for semi-continuous measurement of gas-phase NH_3.
- Air monitoring supersites with sampling and analytic technologies for high-frequency measurement of key reactants and products associated with inorganic and organic aerosol production should be developed and located in source regions of agricultural emissions.
- A multiagency field campaign should be conducted in the Midwest to develop a robust data set for evaluating the impact of agricultural emissions on regional air quality.

Acknowledgements

- Rao Kotamarthi (Argonne) for 1-D Model experiments.
- The support and encouragement of Dr. Ray Knighton, National Program Leader - Air Quality, USDA-CSREES.

* This material is based upon work supported by the National Research Initiative Air Quality Program of the Cooperative State Research, Education, and Extension Service, U.S. Department of Agriculture, under Agreement No. 2005-05108. Any opinions, findings, conclusions, or recommendations expressed in this publication are those of the author(s) and do not necessarily reflect the view of the U.S. Department of Agriculture.