

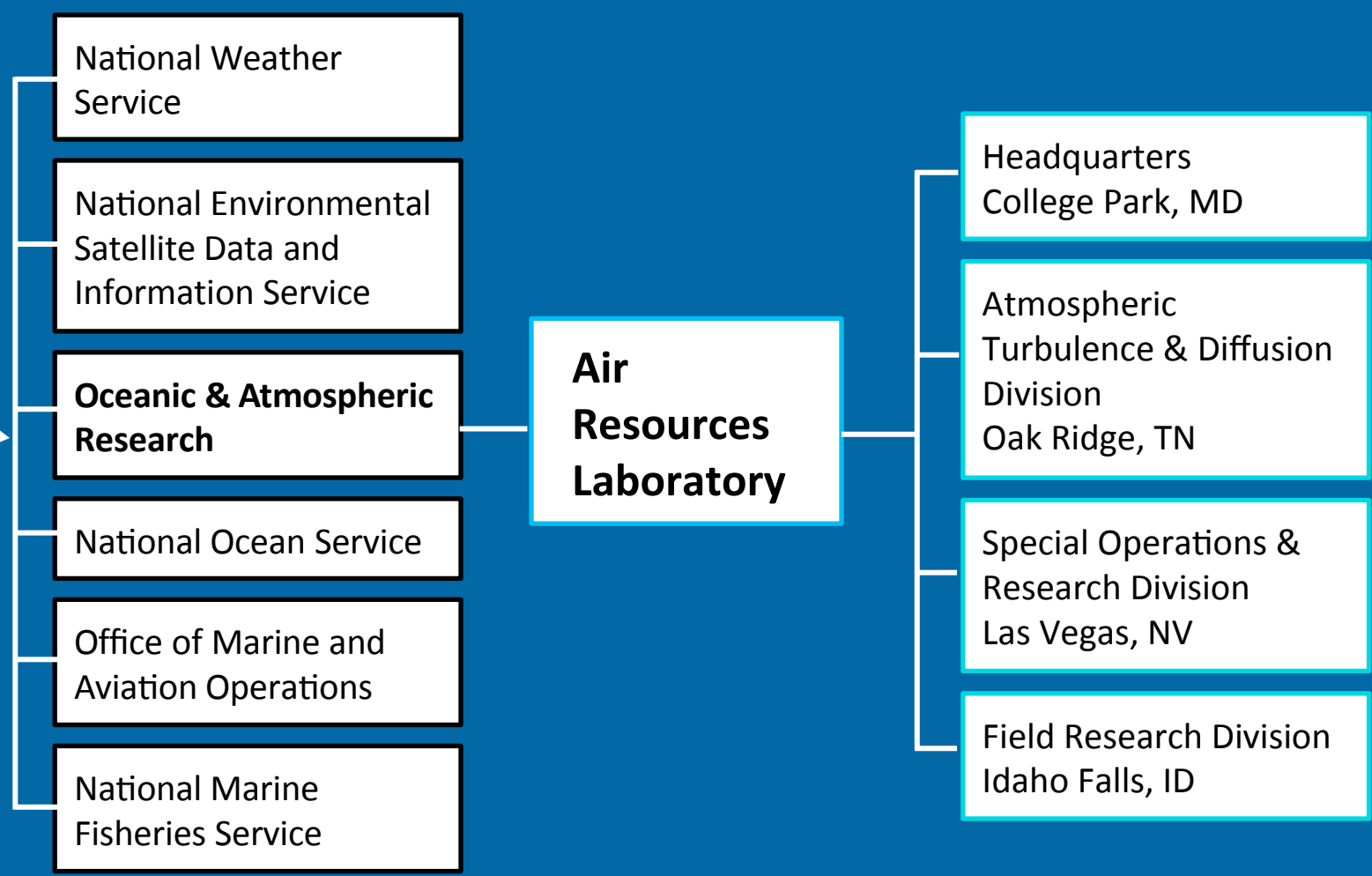


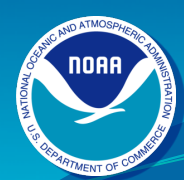
Ammonia Research NOAA Air Resources Laboratory

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¹National Oceanic and Atmospheric Administration
Air Resources Laboratory
Atmospheric Turbulence and Diffusion Division
Oak Ridge TN

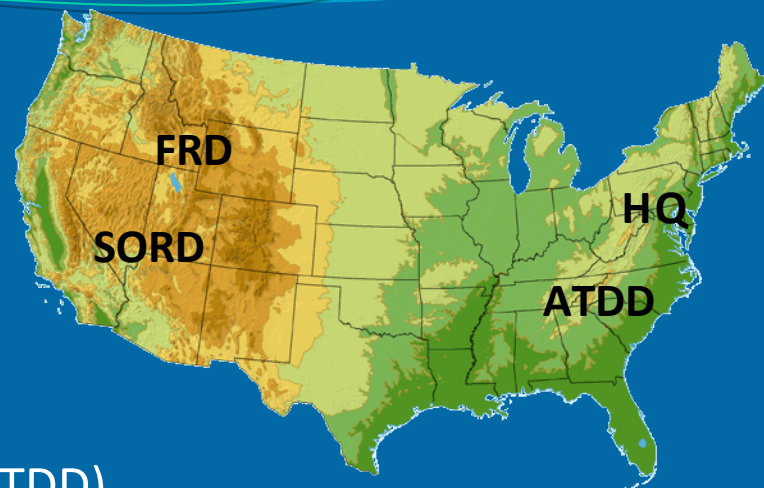
²National Oceanic and Atmospheric Administration
Air Resources Laboratory Headquarters
College Park MD





Headquarters (HQ)

- Atmospheric Dispersion and Boundary Layer Characterization
- Atmospheric Chemistry and Deposition
- Climate Observations and Analyses



Atmospheric Turbulence & Diffusion Division (ATDD)

- Atmospheric Dispersion and Boundary Layer Characterization
- Atmospheric Chemistry and Deposition
- Climate Observations and Analyses

Field Research Division (FRD)

- Atmospheric Dispersion and Boundary Layer Characterization
- Substantial site support for DOE

Special Operations & Research Division (SORD)

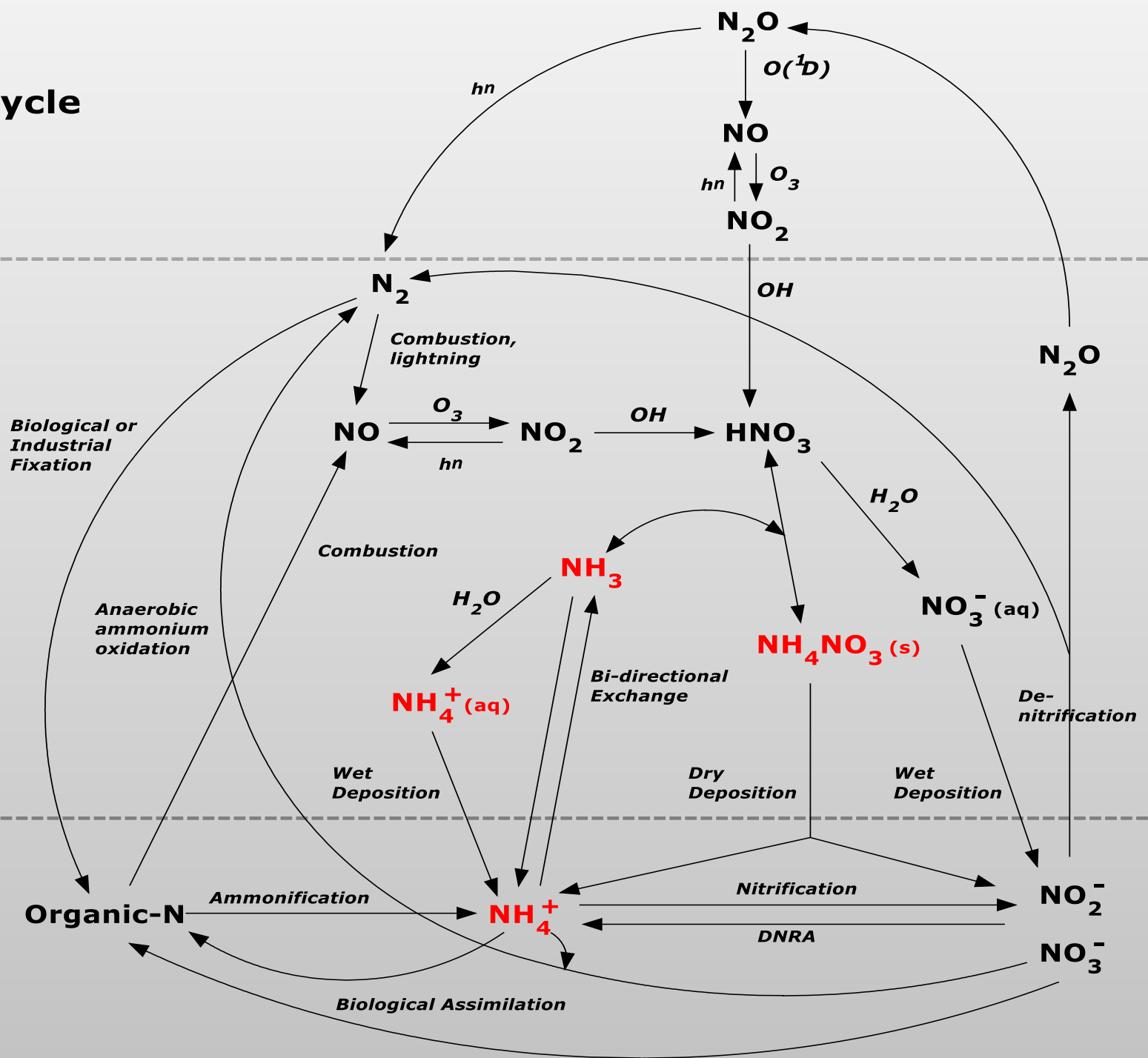
- Atmospheric Dispersion and Boundary Layer Characterization
- Substantial site support for DOE

Nitrogen Cycle

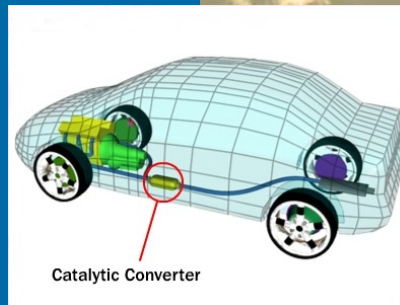
Stratosphere

Troposphere

Biosphere



Sources of Atmospheric NH_3





Why Ammonia?

- Important component of global N cycle (Galloway, 2003)
- Only gaseous alkaline substance in the atmosphere
- At high concentrations can directly damage vegetation (Krupa, 2003)
- Deposition of NH_3 , along with other reactive N, can alter the N status of aquatic and terrestrial ecosystems
- Participates in the production and growth of PM



National Air Quality Forecast Capability (NAQFC) for O₃ and PM_{2.5}

Meteorological Model

- ❖ North American Model (NAM) - 12 km

Emission projection

- ❖ Area sources use US EPA 2011 NEI v1
- ❖ Point sources use biennial CEM and latest DoE energy consumption outlook
- ❖ Mobile sources use US EPA 2012 Cross State Air Pollution Rule MOBILE6 output scaled by EPA AQS monitored trends
- ❖ BEIS3 v3.14 Biogenic Emissions
- ❖ Intermittent sources: dust and wildfire

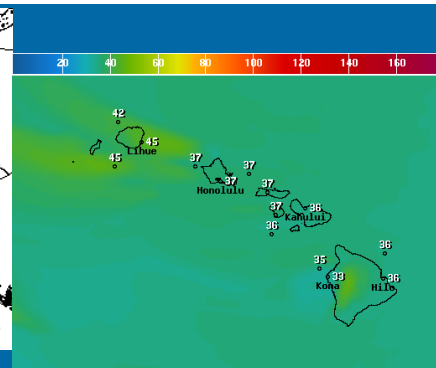
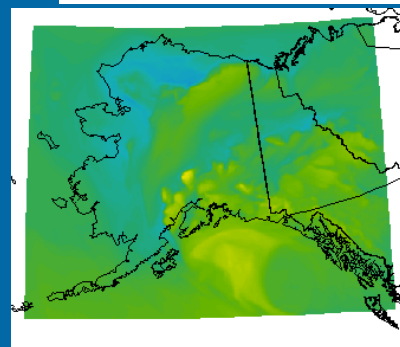
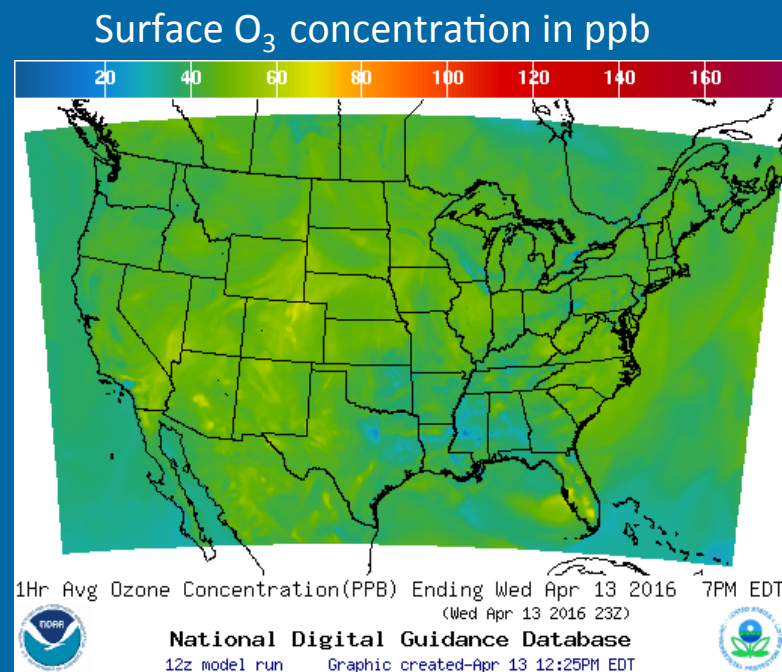
Air Quality chemistry-transport Model

- ❖ US EPA CMAQ v4.6 – 12 km

NAQFC 48 h forecast online:

- ❖ O₃ for CONUS, AK and HI
- ❖ PM_{2.5} for CONUS

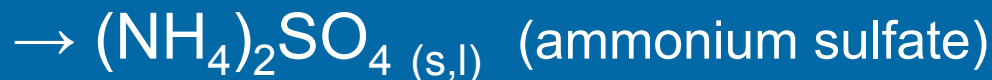
Air Resources Laboratory

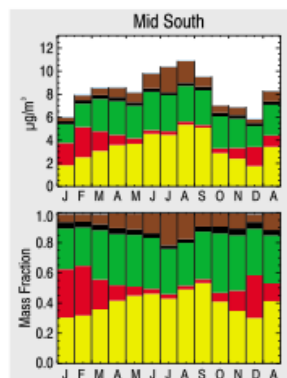
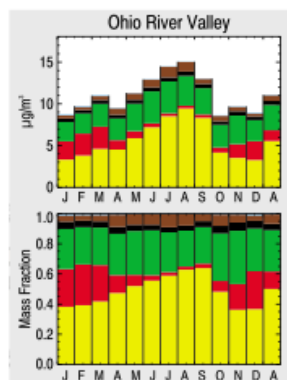
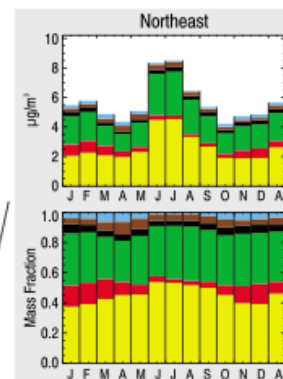
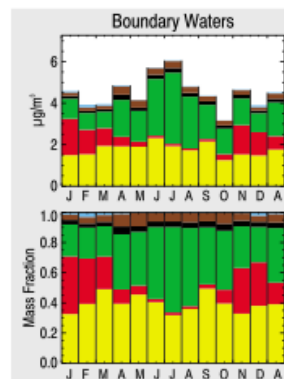
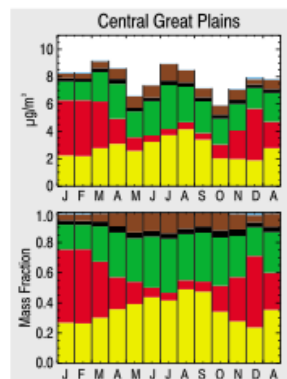


airquality.weather.gov

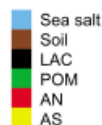
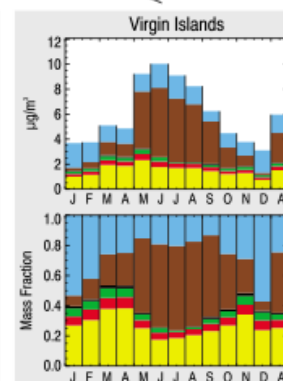
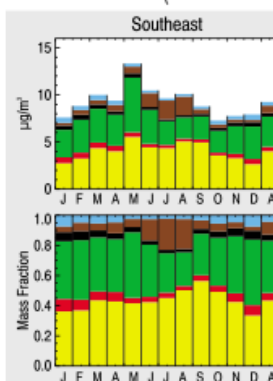
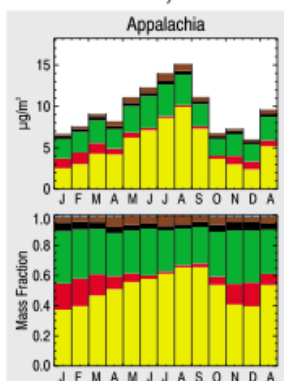
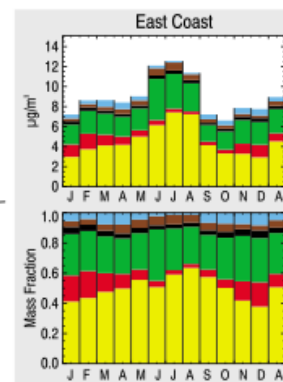
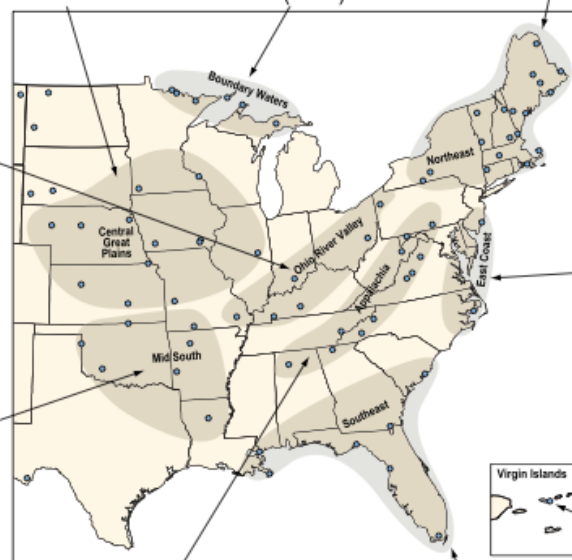


Ammonia reacts with strong acids in the atmosphere to form ammonium salts ...





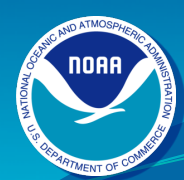
IMPROVE: Eastern U.S. (rural)





Ammonia-Related Research Activities in the NOAA Air Resources Laboratory

- Measurements – increase knowledge base of NH_3 concentrations and flux measurements over diverse landscapes and in a variety of environmental conditions
- Data analyses – increase our understanding of NH_3 spatial and temporal variations and trends
- Process modeling – use specialized models in conjunction with measurements to increase our understanding of controlling processes
- 3-D air quality modeling – accurately simulate the large-scale distribution of NH_x (better $\text{PM}_{2.5}$ forecasts)



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Evaluating ammonia (NH_3) predictions in the NOAA National Air Quality Forecast Capability (NAQFC) using *in situ* aircraft, ground-level, and satellite measurements from the DISCOVER-AQ Colorado campaign

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HIGHLIGHTS

- *In situ* aircraft measurements in summer 2014 suggest the NAQFC CMAQ model underestimated NH_3 in NE Colorado by a factor of 2.7.
- Ground-level monitors and satellite retrievals produced a similar results.
- The underestimation of NH_3 vapor was not accompanied by a comparable underestimation of particulate NH_4^+ .
- Seasonal patterns measured at an AMoN site in the region suggest that the underestimation of NH_3 is not limited to summer.

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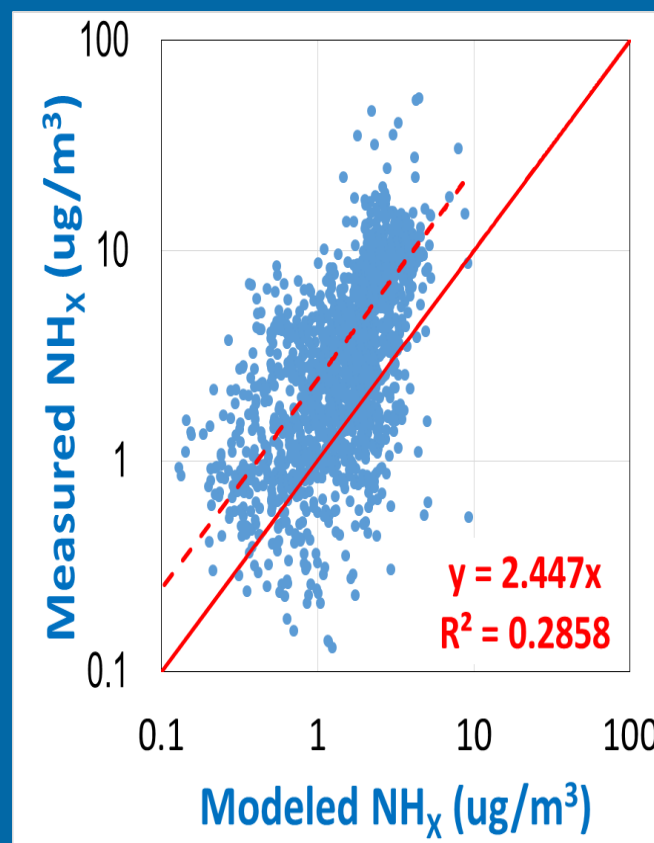
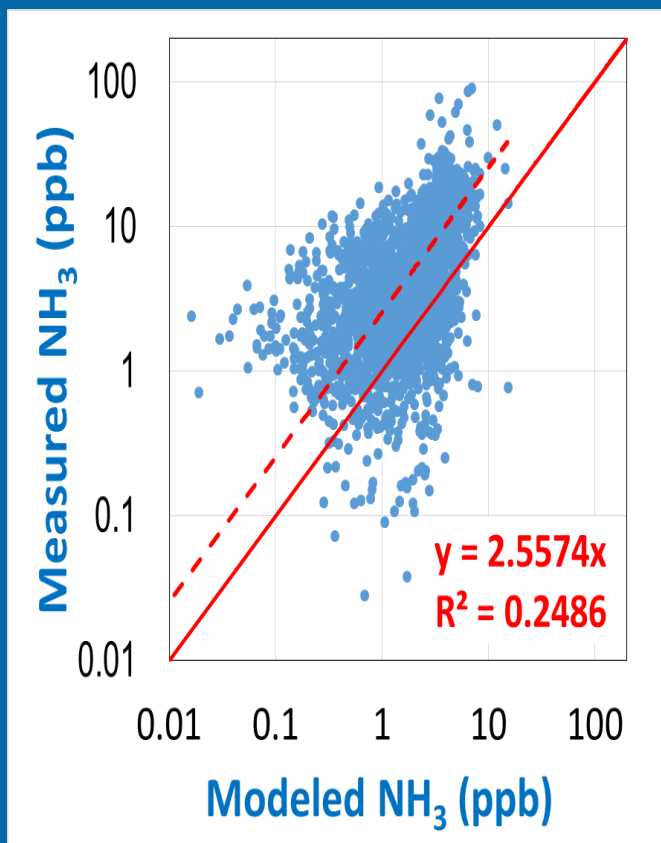
ABSTRACT

The U.S. National Oceanic and Atmospheric Administration (NOAA) is responsible for forecasting elevated levels of air pollution within the National Air Quality Forecast Capability (NAQFC). The current research uses measurements gathered in the DISCOVER-AQ Colorado field campaign and the concurrent Front Range Air Pollution and Photochemistry Experiment (FRAPPE) to test performance of the NAQFC CMAQ modeling framework for predicting NH_3 . The DISCOVER-AQ and FRAPPE field campaigns were carried out in July and August 2014 in Northeast Colorado. Model predictions are compared with measurements of NH_3 gas concentrations and the NH_4^+ component of fine particulate matter concentrations measured directly by the aircraft in flight. We also compare CMAQ predictions with NH_3 measurements from ground-based monitors within the DISCOVER-AQ Colorado geographic domain, and from the Tropospheric Emission Spectrometer (TES) on the Aura satellite.

In situ aircraft measurements carried out in July and August of 2014 suggest that the NAQFC CMAQ model underestimated the NH_3 concentration in Northeastern Colorado by a factor of ~2.7 (NMB = −63%). Ground-level monitors also produced a similar result. Average satellite-retrieved NH_3 levels also exceeded model predictions by a factor of 1.5–4.2 (NMB = −33 to −76%). The underestimation of NH_3 was not accompanied by an underestimation of particulate NH_4^+ , which is further controlled by factors including acid availability, removal rate, and gas-particle partition. The average measured concentration of NH_4^+ was close to the average prediction (NMB = +18%).

Seasonal patterns measured at an AMoN site in the region suggest that the underestimation of NH_3 is not due to the seasonal allocation of emissions, but to the overall annual emissions estimate. The underestimation of NH_3 varied across the study domain, with the largest differences occurring in a region of intensive agriculture near Greeley, Colorado, and in the vicinity of Denver. The NAQFC modeling framework did not include a recently developed bidirectional flux algorithm for NH_3 , which has shown to considerably improve NH_3 modeling in agricultural regions. The bidirectional flux algorithm, however,

NAQFC predictions compared with *in situ* aircraft measurements (DISCOVER-AQ Colorado, summer 2014, <1 km altitude)



Solid line = 1:1 slope

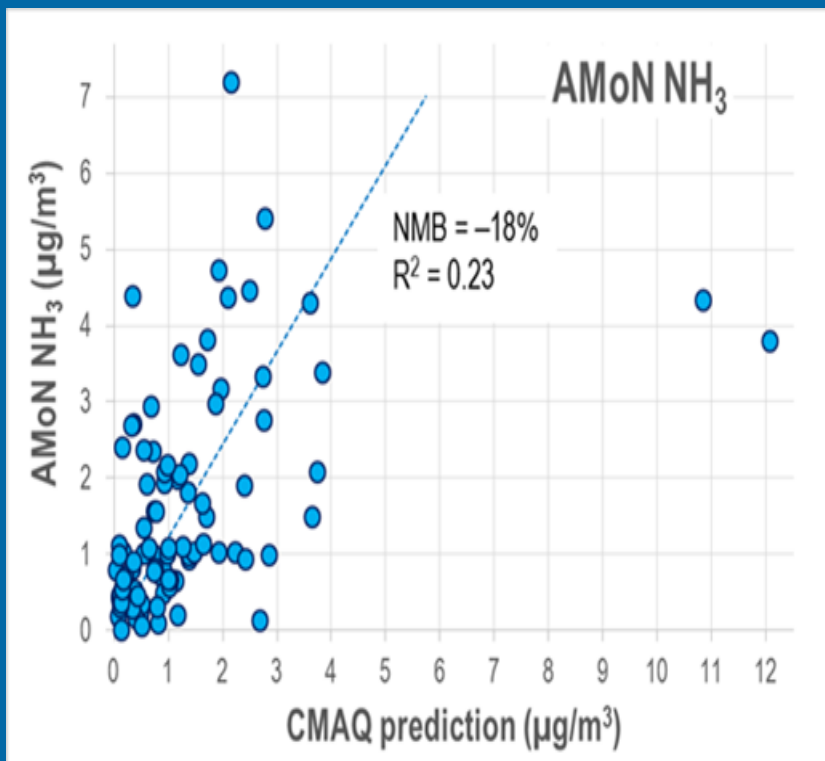
Dotted line = 1:1 line displaced by mean bias

NH_x = total ammonium (NH_3 & NH_4^+)

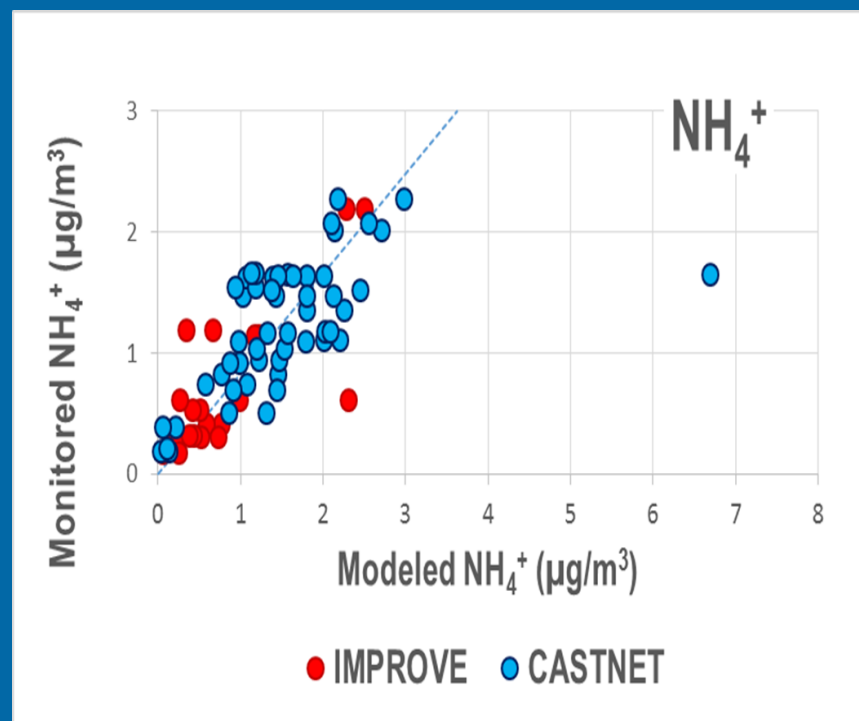
(Source: Battye et al, 2016)

NAQFC predictions compared with ground level measurements

AMoN NH_3



CASTNet and IMPROVE NH_4^+

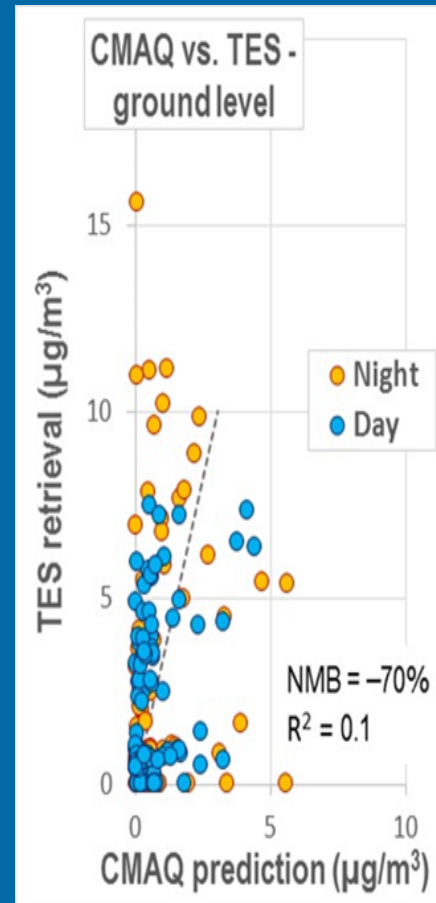
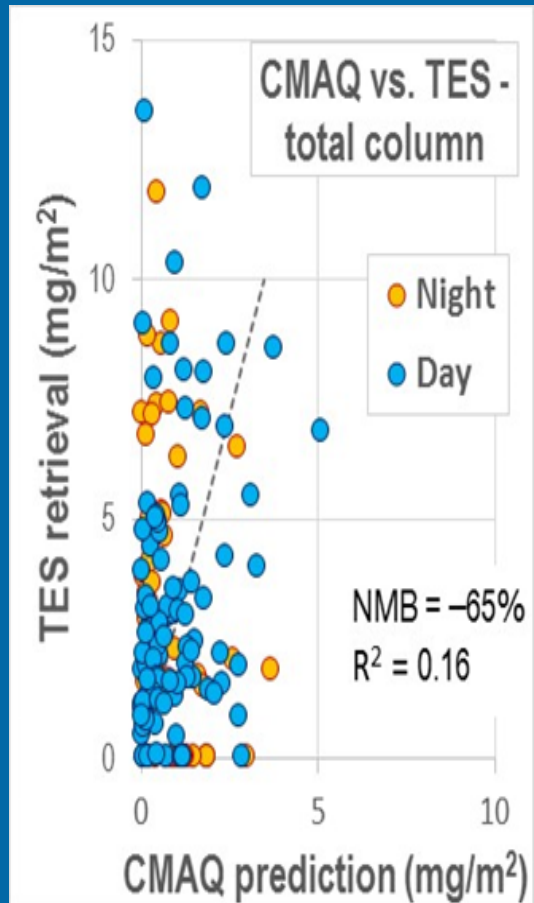


Source: Battye et al

NAQFC predictions compared with TES retrievals

Total atmospheric column

Ground-level concentration





Findings from Battye et al. (2016)

- Aircraft measurements suggest NAQFC-CMAQ underestimates NH_3 in agricultural regions of Colorado and California
- Measured spatial and temporal variations in NH_3 are larger than the variations in model predictions
- Ground-based measurements and TES retrievals were too sparse to evaluate the model for the period analyzed (July 2011)

Future work

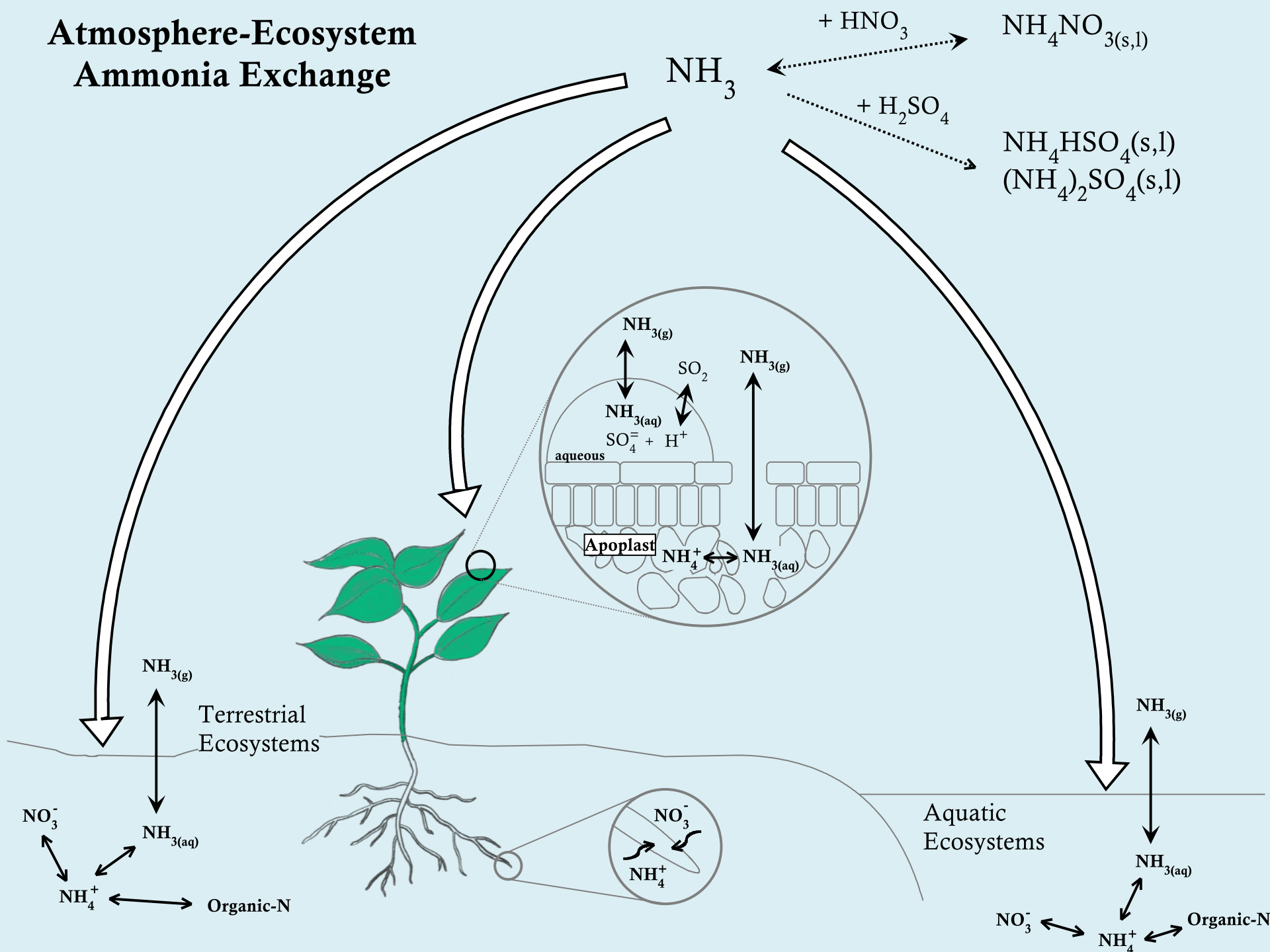
- AIRS or IASI satellite retrievals may provide a method of filling in the gaps

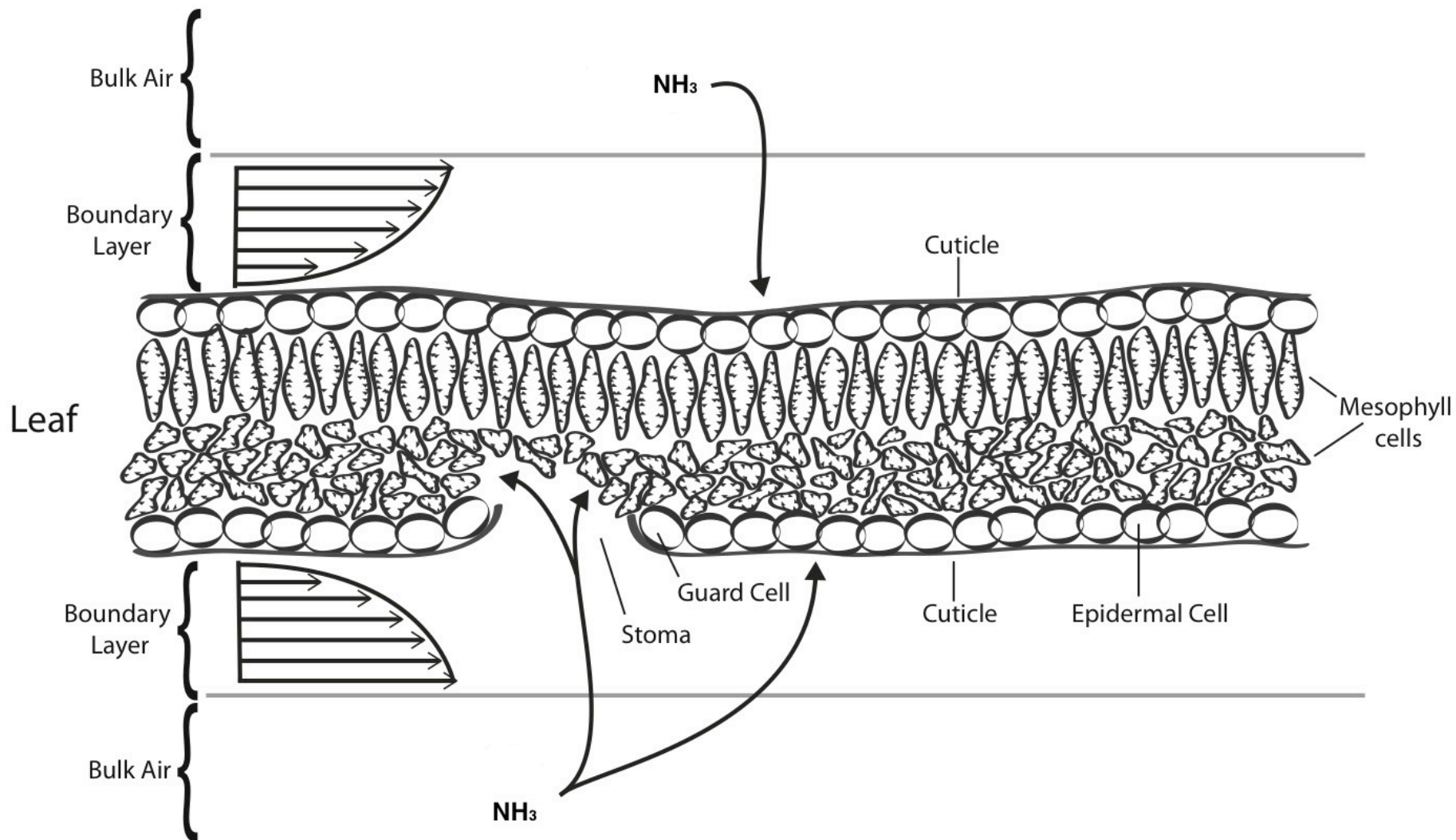


Challenges of Measuring NH_3

- Concentrations generally near or less than 1 ppbv, except near sources.
- Adsorbs onto surfaces, especially those that are wetted or even partially covered with water molecules, potentially resulting in memory effects.
- Partitions between gas-aerosol-hydrometeor phases, so that multiphase measurements are necessary to fully characterize.
- Reduced nitrogen species are usually not as abundant as oxidized nitrogen species ($\text{NO}_y = \text{NO}, \text{NO}_2, \text{HNO}_3$, etc.), making it difficult to detect NH_3 against the NO_y background.

Atmosphere-Ecosystem Ammonia Exchange





SEARCH

SouthEastern

Aerosol

Research

and

CHaracterization

Study



ELECTRIC POWER
RESEARCH INSTITUTE

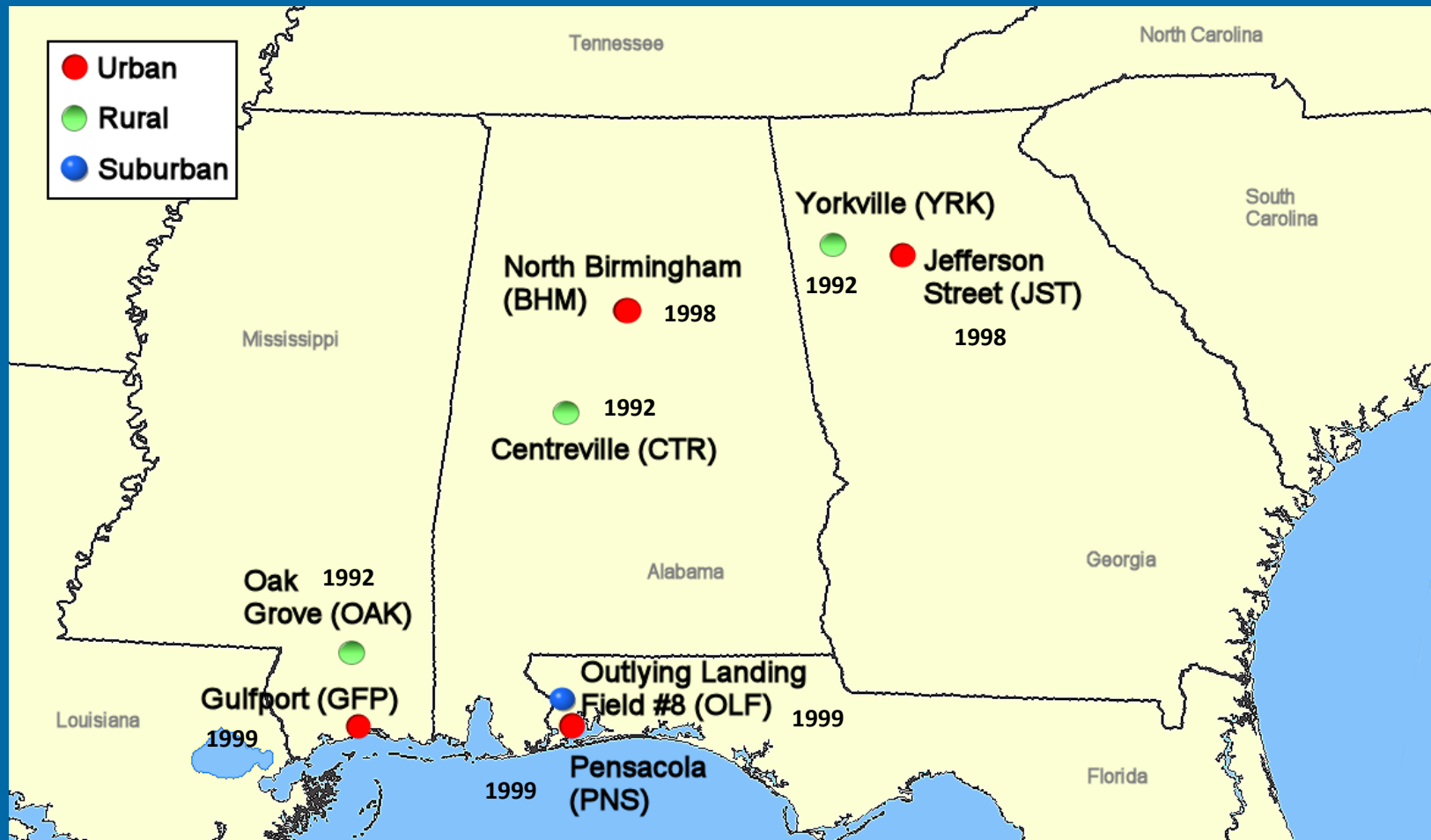
Jefferson Street, Atlanta (JST)



Yorkville, Georgia (YRK)



SEARCH Measurement Network





SEARCH Measurements

- **Filter-Based Particles and Gases (24-hour)**

- FRM: $PM_{2.5}$
- PCM and Dichot: $PM_{2.5}$, $PM_{10-2.5}$ mass and speciation (TC, OC, BC, NH_4^+ , NO_3^- , SO_4^{2-})
- NH_3 (citric acid denuder)

- **Continuous Particles (5-min to 1-hr)**

- TEOM: $PM_{2.5}$ mass
- Sunset Labs: OC/EC/TC
- Aethelometer: BC
- SEARCH/ARA: NH_4^+ , NO_3^-
- Modified HSPH: SO_4^{2-}

- **Trace Gases (5-min)**

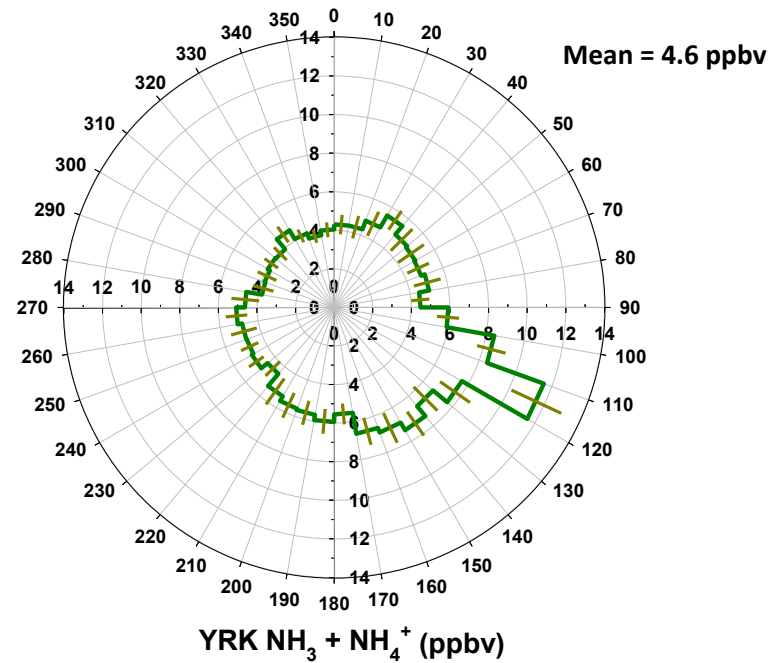
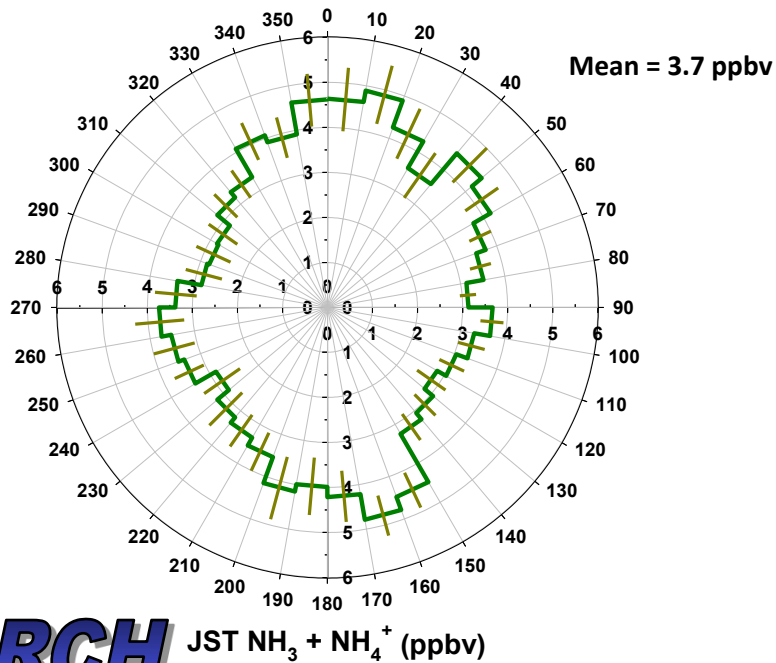
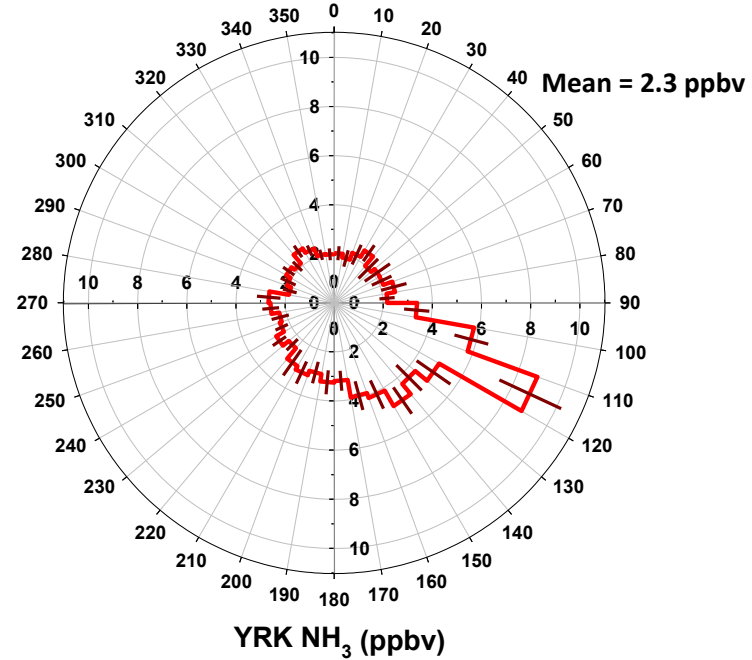
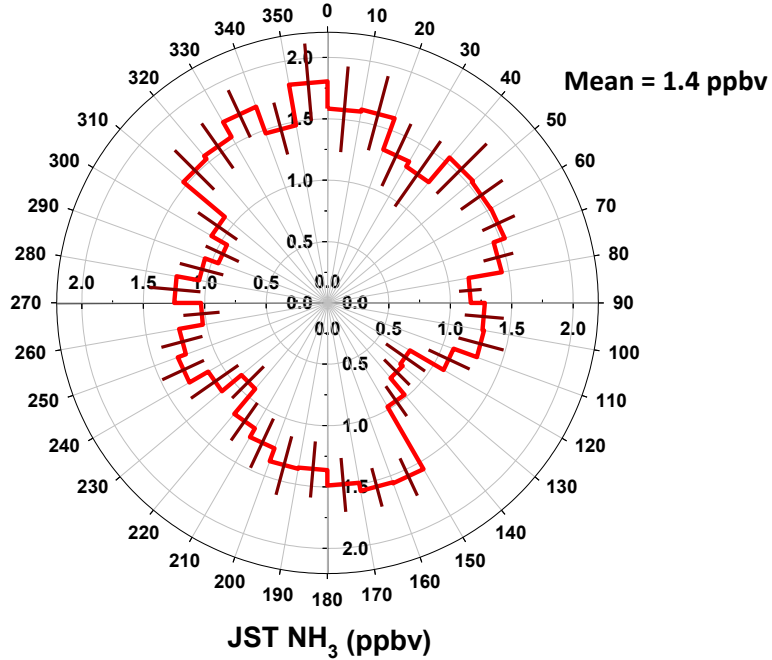
- O_3 , NO, NO_2 , NO_y , HNO_3 , SO_2 , CO, CO_2
- NH_3 (3 sites)

- **Meteorology (5-min)**

- WS, WD, T, RH, BP, SR, rainfall

- **Mercury**

- Continuous Hg, Hg^P , RGM (3 sites)
- Weekly or daily wet deposition (5 sites)



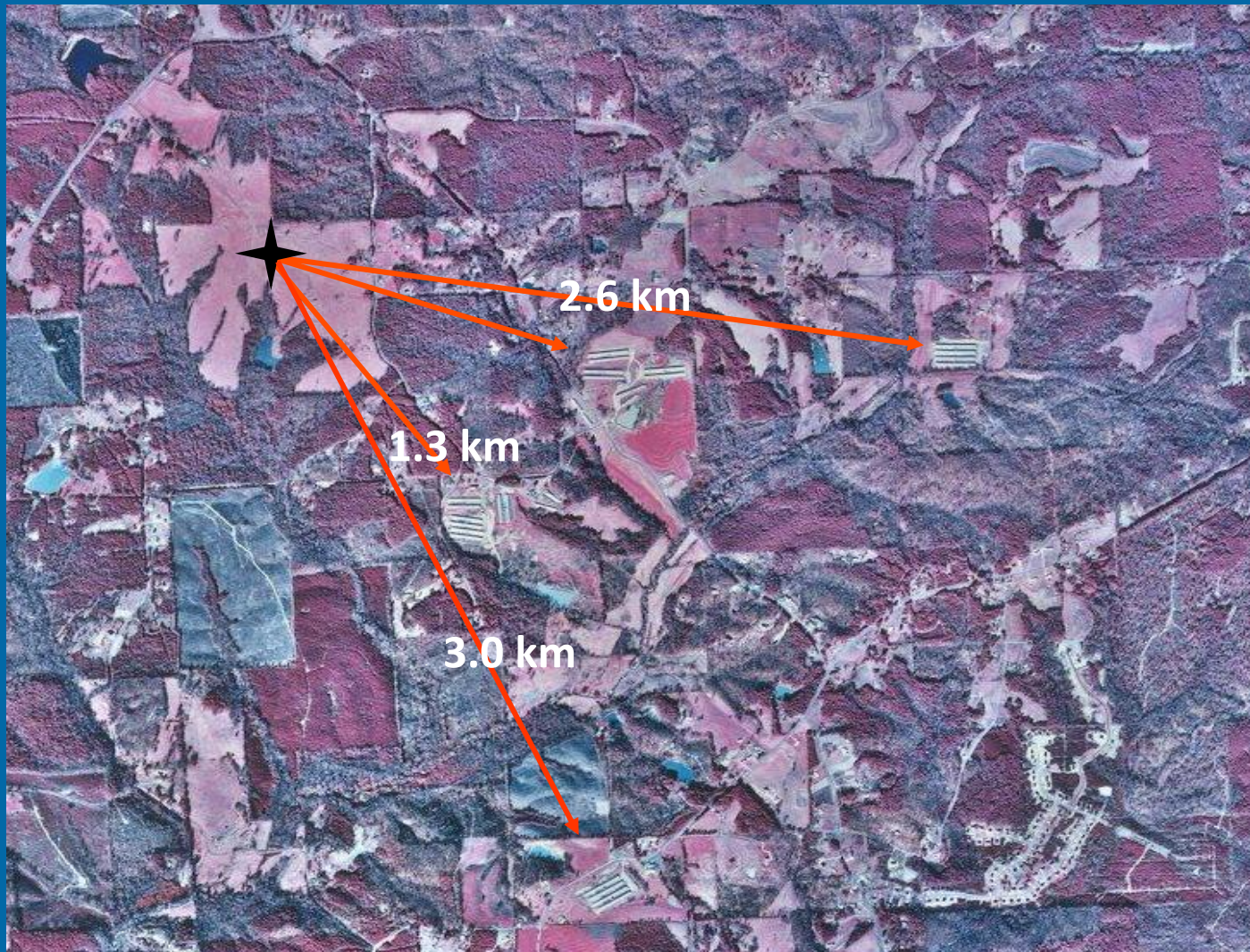
SEARCH

Hourly-Avg NH₃ Values > 30 ppbv at YRK

Datetime	NH ₃ (ppbv) YRK	NH ₄ ⁺ (ppbv) YRK	WindDir (deg) YRK	NH ₃ /NH _x (mol/mol) YRK		NH ₃ (ppbv) JST	NH ₄ ⁺ (ppbv) JST	NH ₃ /NH _x (mol/mol) JST
11/29/2007 07:00	46.3	1.4	139.7	0.971		1.8	0.7	0.724
7/14/2007 05:00	41.6	3.3	115.3	0.926		1.5	2.5	0.377
10/14/2007 20:00	39.2	5.8	117.8	0.871		1.2	3.7	0.247
7/14/2007 06:00	38.3	3.5	112.1	0.917		1.5	2.7	0.354
10/15/2007 18:00	36.7	2.8	110.2	0.929		< DL	2.5	0.020
10/8/2007 00:00	32.0	3.7	113.5	0.896		1.9	1.5	0.558
8/24/2007 07:00	32.0	3.6	126.5	0.899		3.8	2.5	0.598
10/15/2007 19:00	31.9	2.6	115.8	0.925		0.4	2.1	0.170
8/27/2007 04:00	31.7	4.7	110.4	0.872		2.7	2.4	0.532



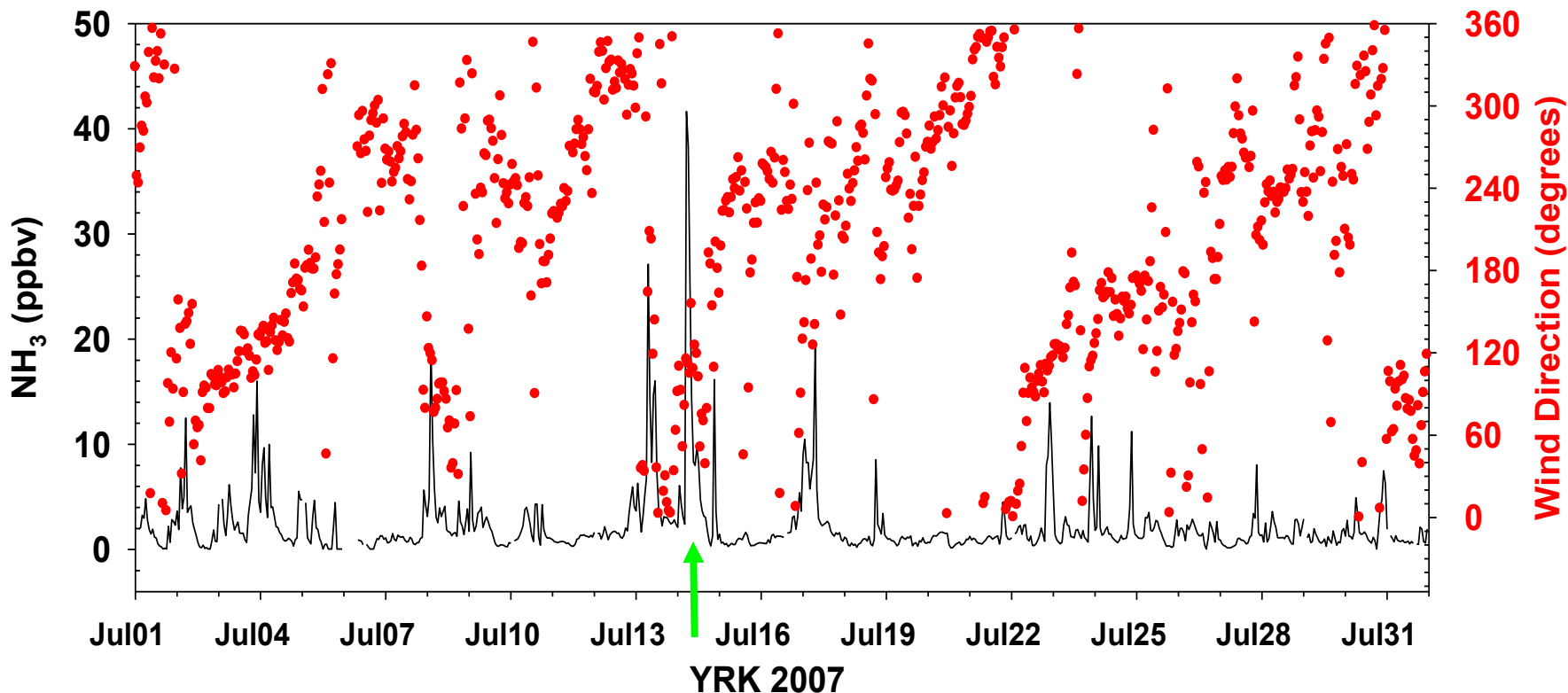
Poultry Houses near YRK



SEARCH

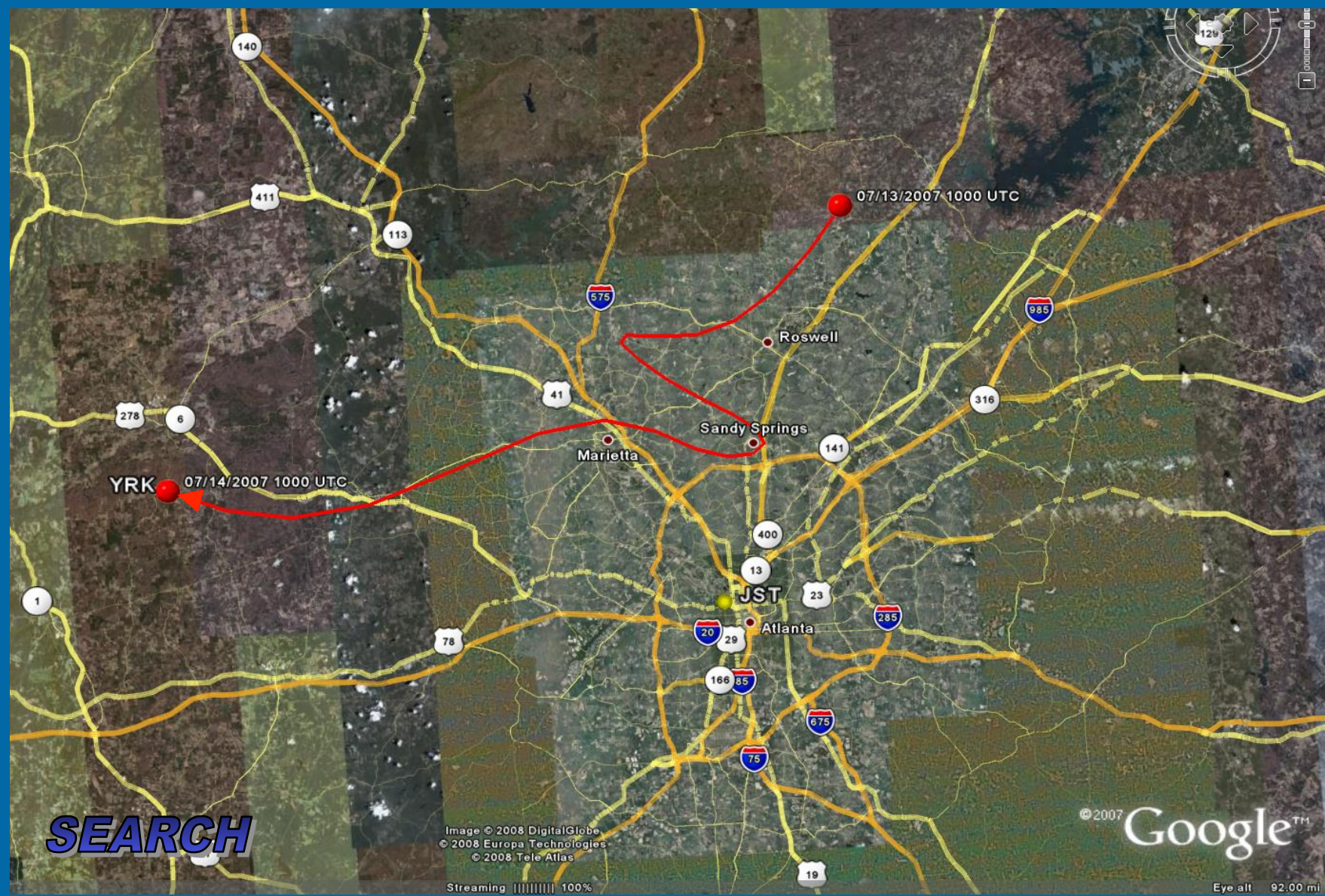
Hourly-Averaged NH_3 and Wind Direction

YRK July 2007





HYSPLIT Back Trajectory July 14, 2007



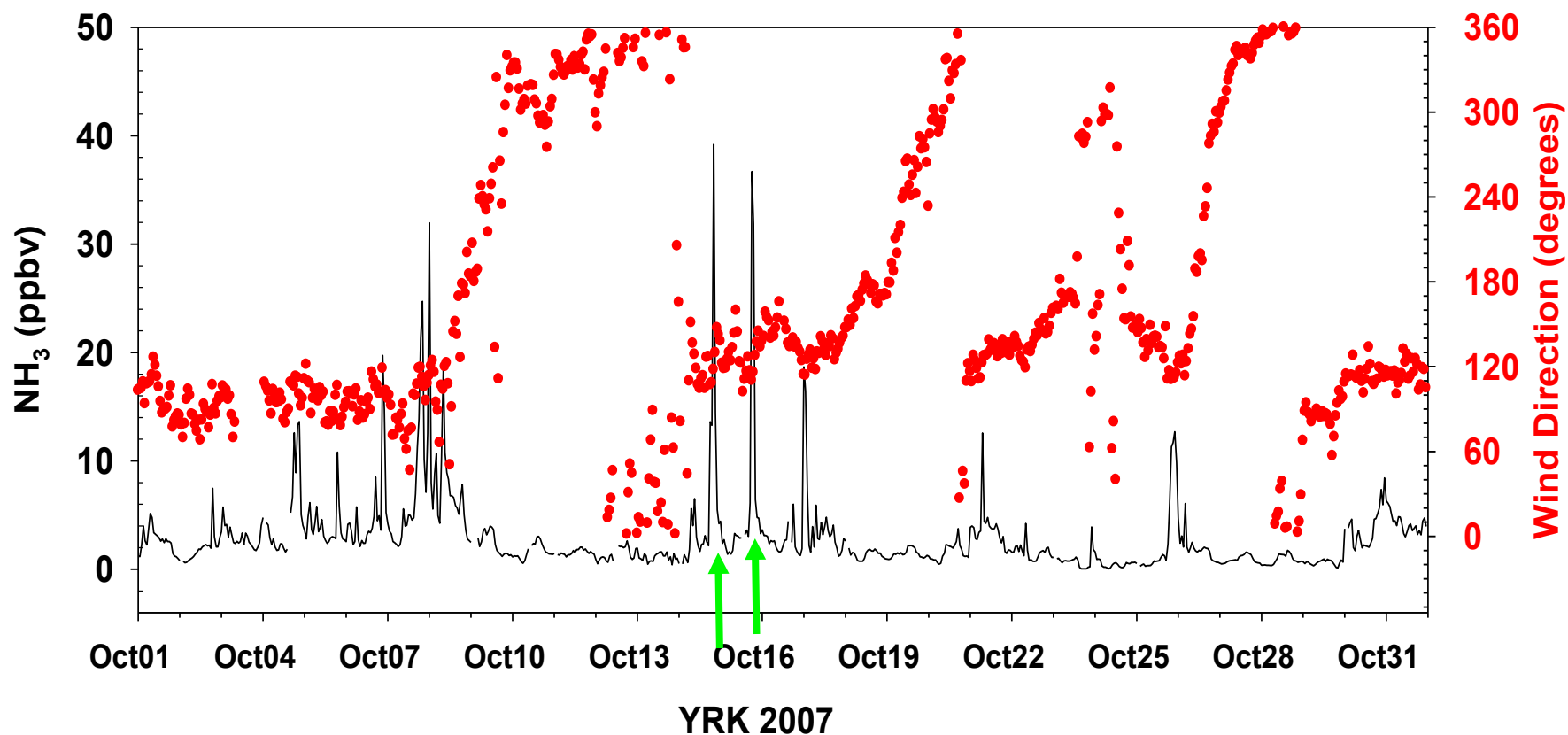


HYSPLIT Back Trajectory July 14, 2007 - Zoom



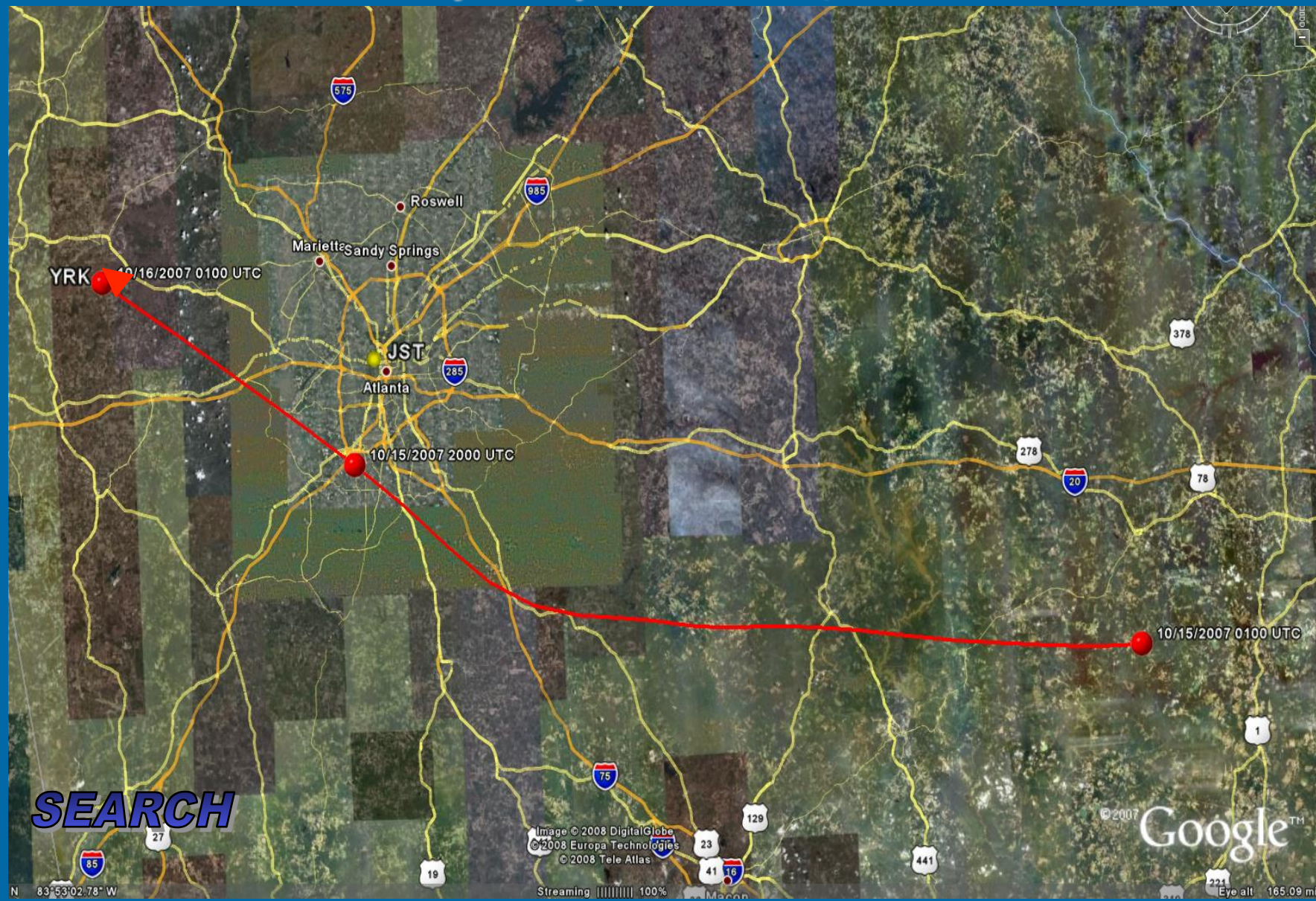
Hourly-Averaged NH_3 and Wind Direction

YRK October 2007





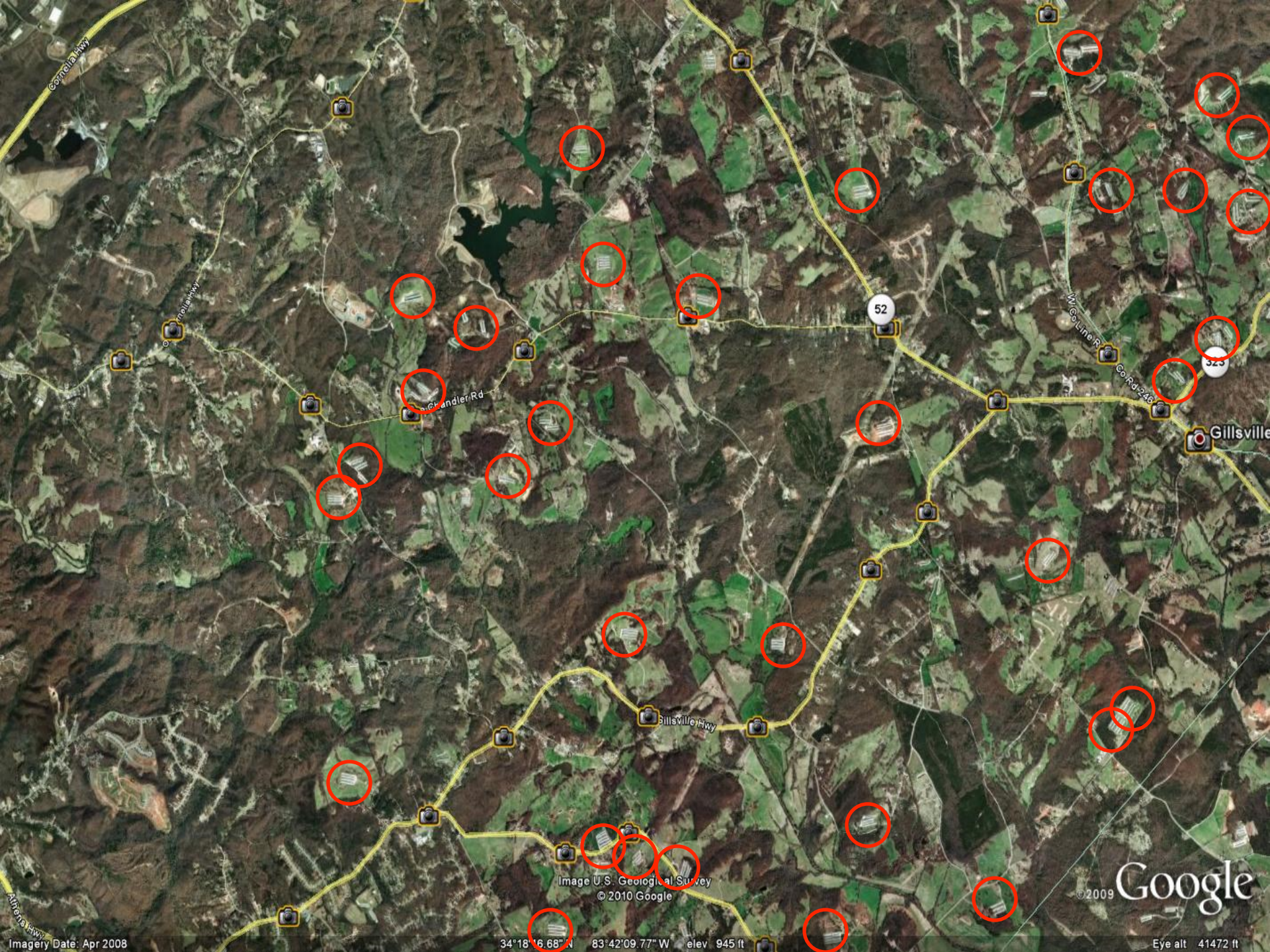
HYSPLIT Back Trajectory October 15, 2007





HYSPLIT Back Trajectory Oct 15, 2007 - Zoom





Corrala Hwy

Trillax Hwy

Chandler Rd

Gillsville Hwy

W. Greene Rd

Go Rd 245

Gillsville

Image U.S. Geological Survey
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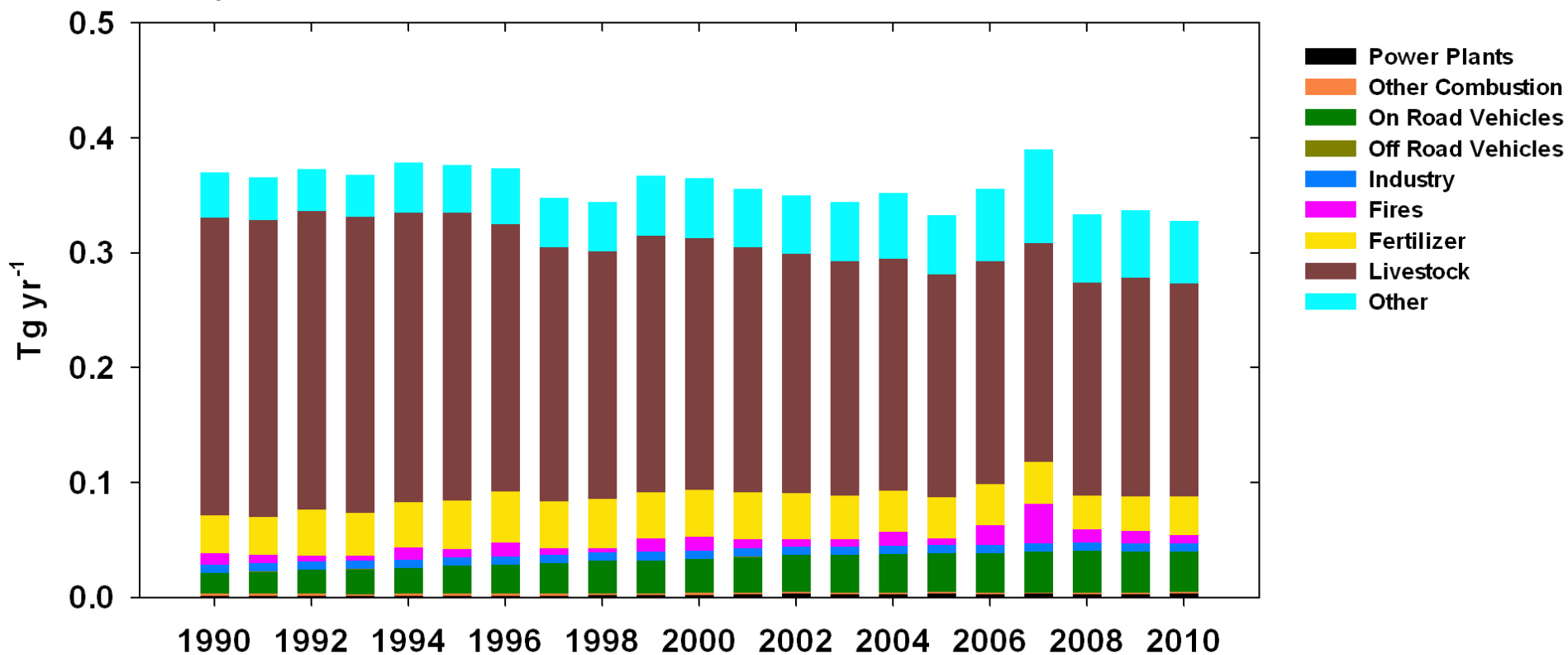
34°18'16.68" N 83°42'09.77" W elev 945 ft

Eye alt 41472 ft

Imagery Date: Apr 2008



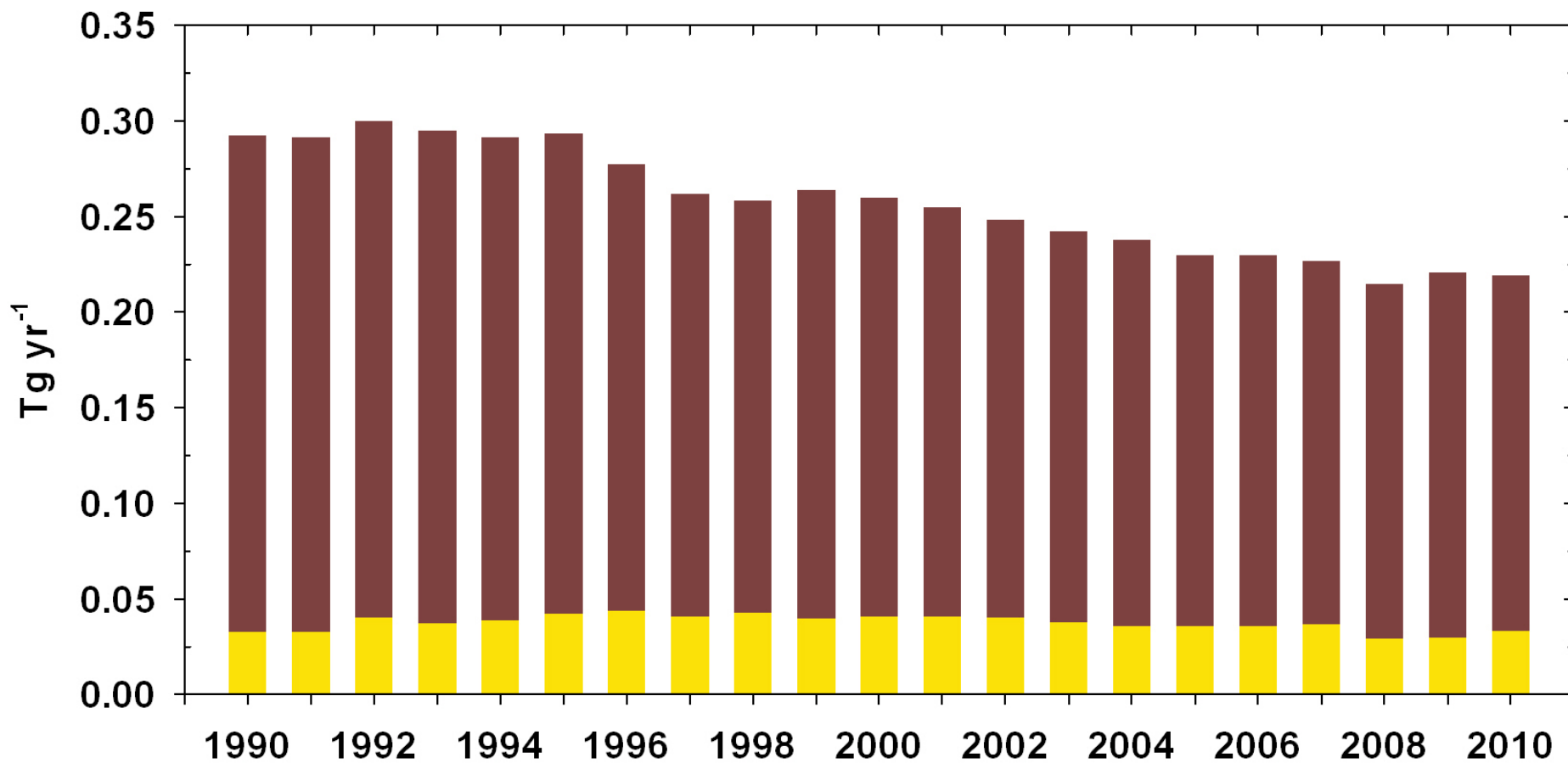
NH₃ Emissions - All Sources - SEARCH States - Xing et al. (2013)



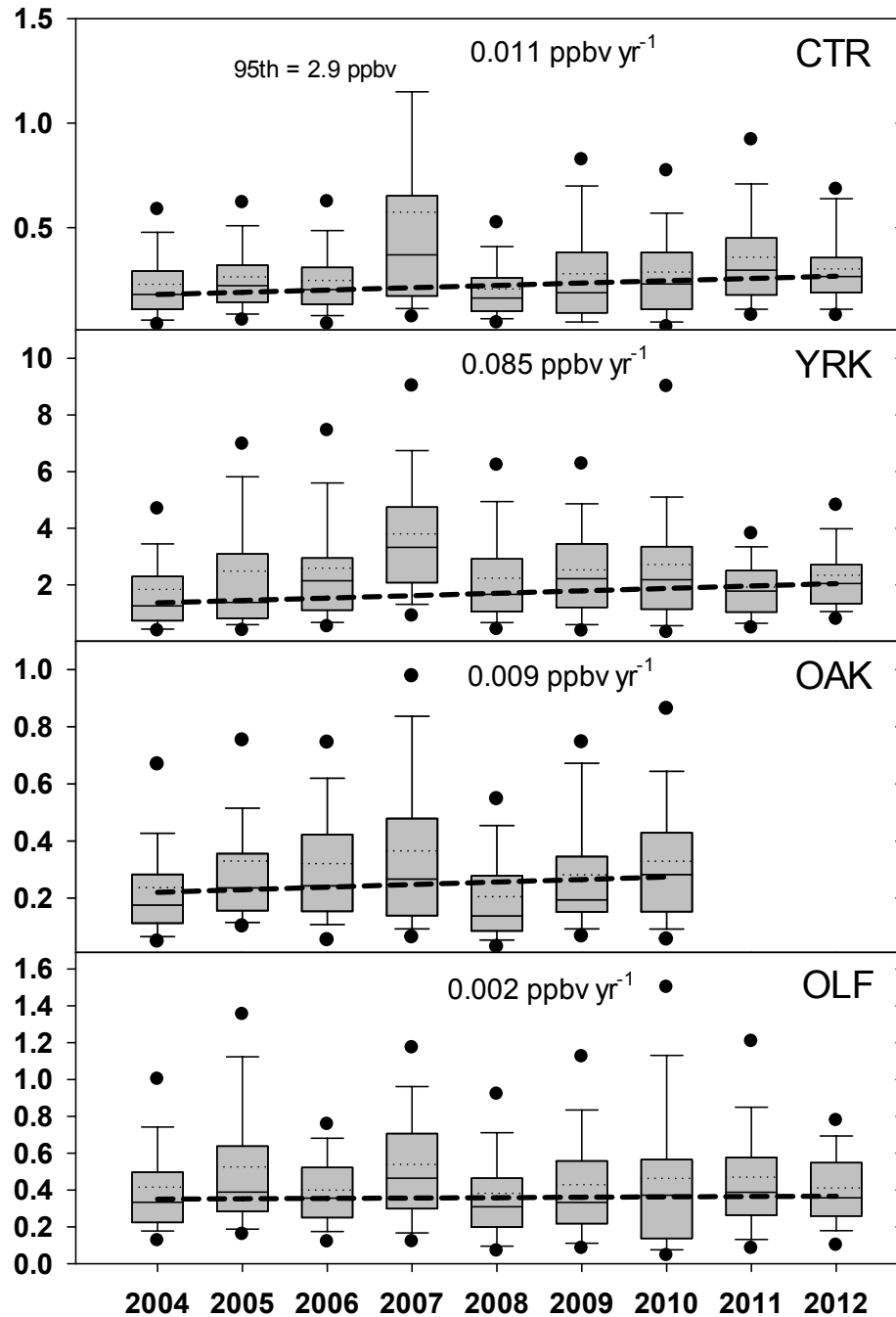
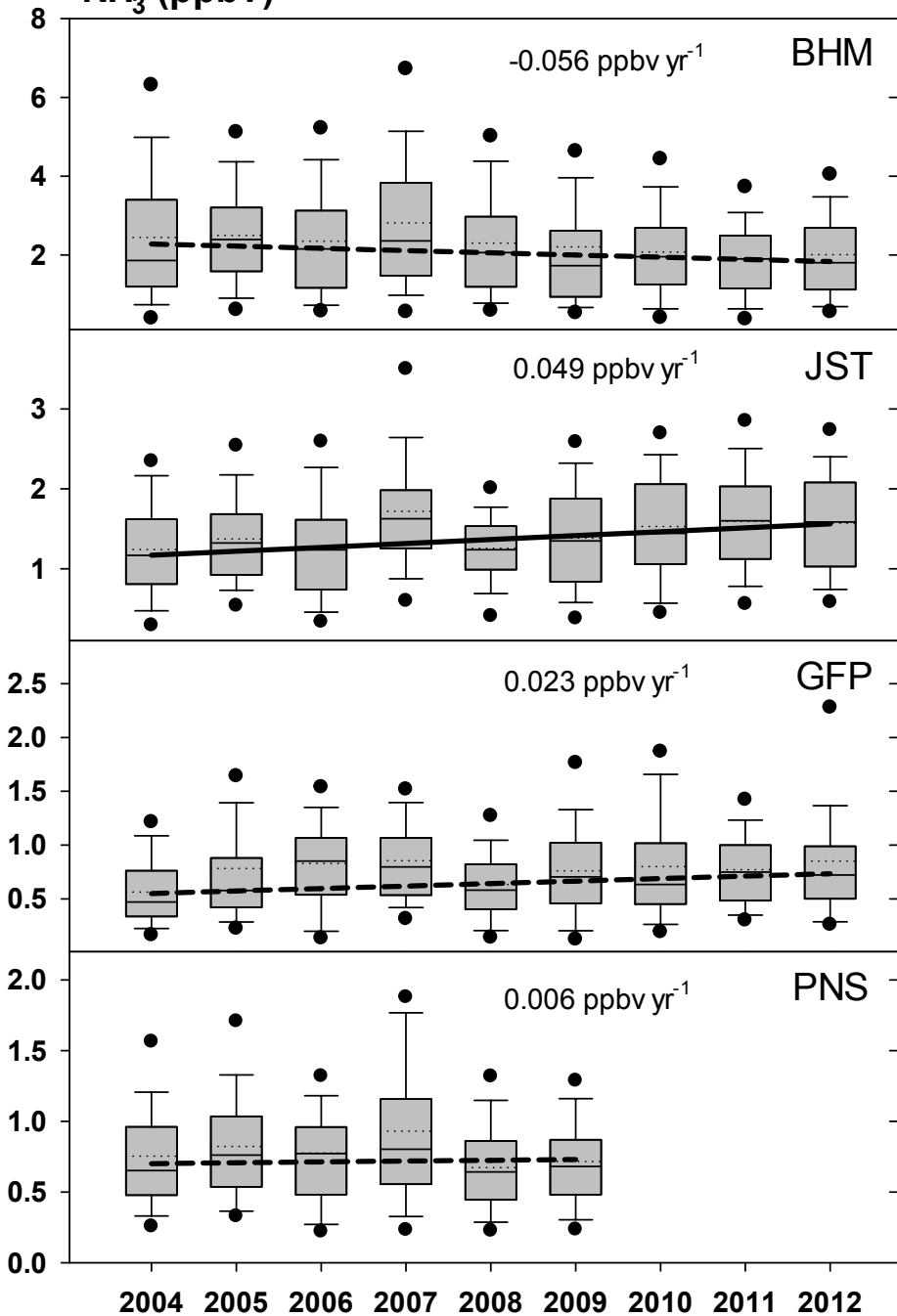
Xing et al. (2013) Historical gaseous and primary aerosol emissions in the United States from 1990 to 2010, Atmos. Chem. Phys., 13, 7531-7549.

Fertilizer
Livestock

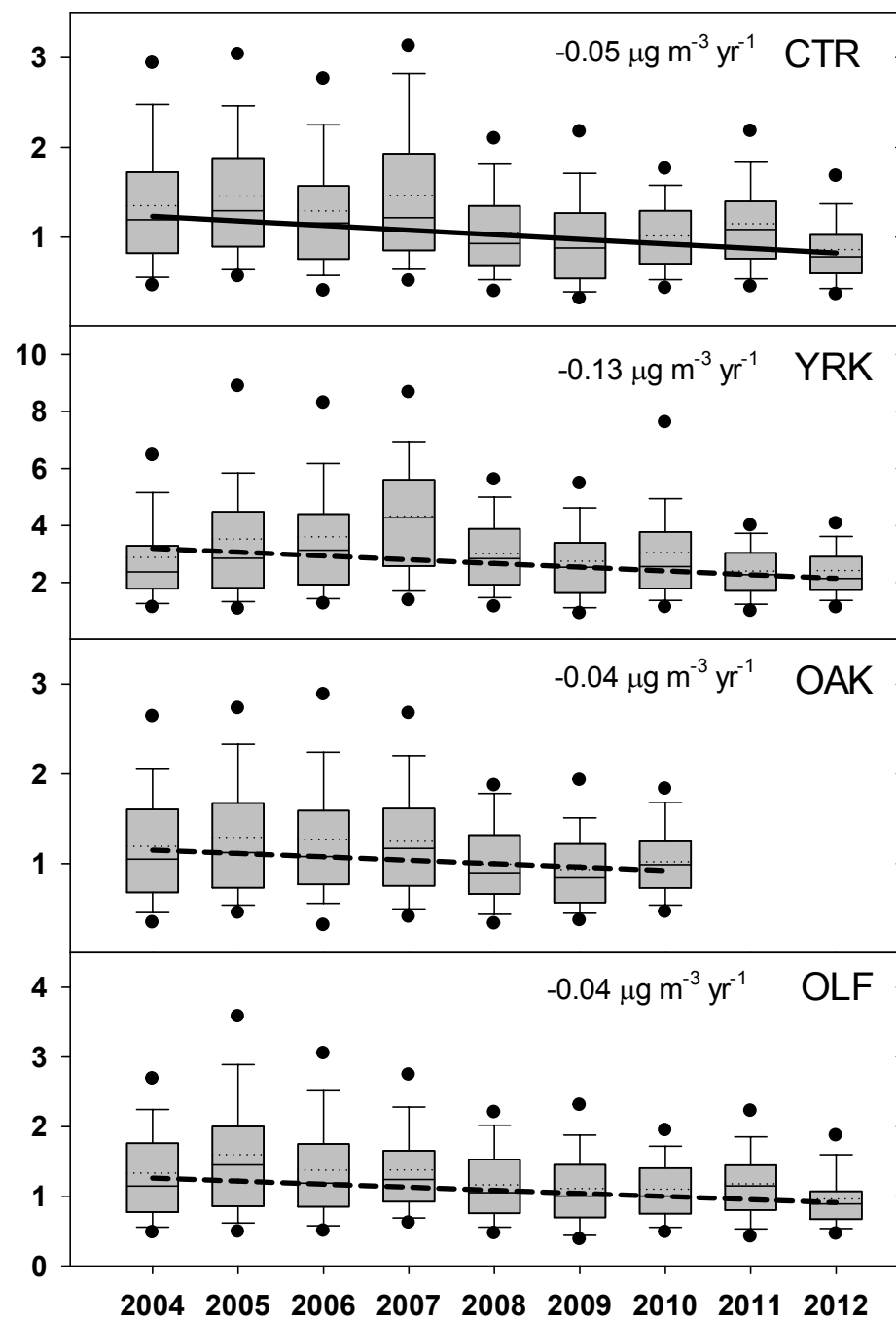
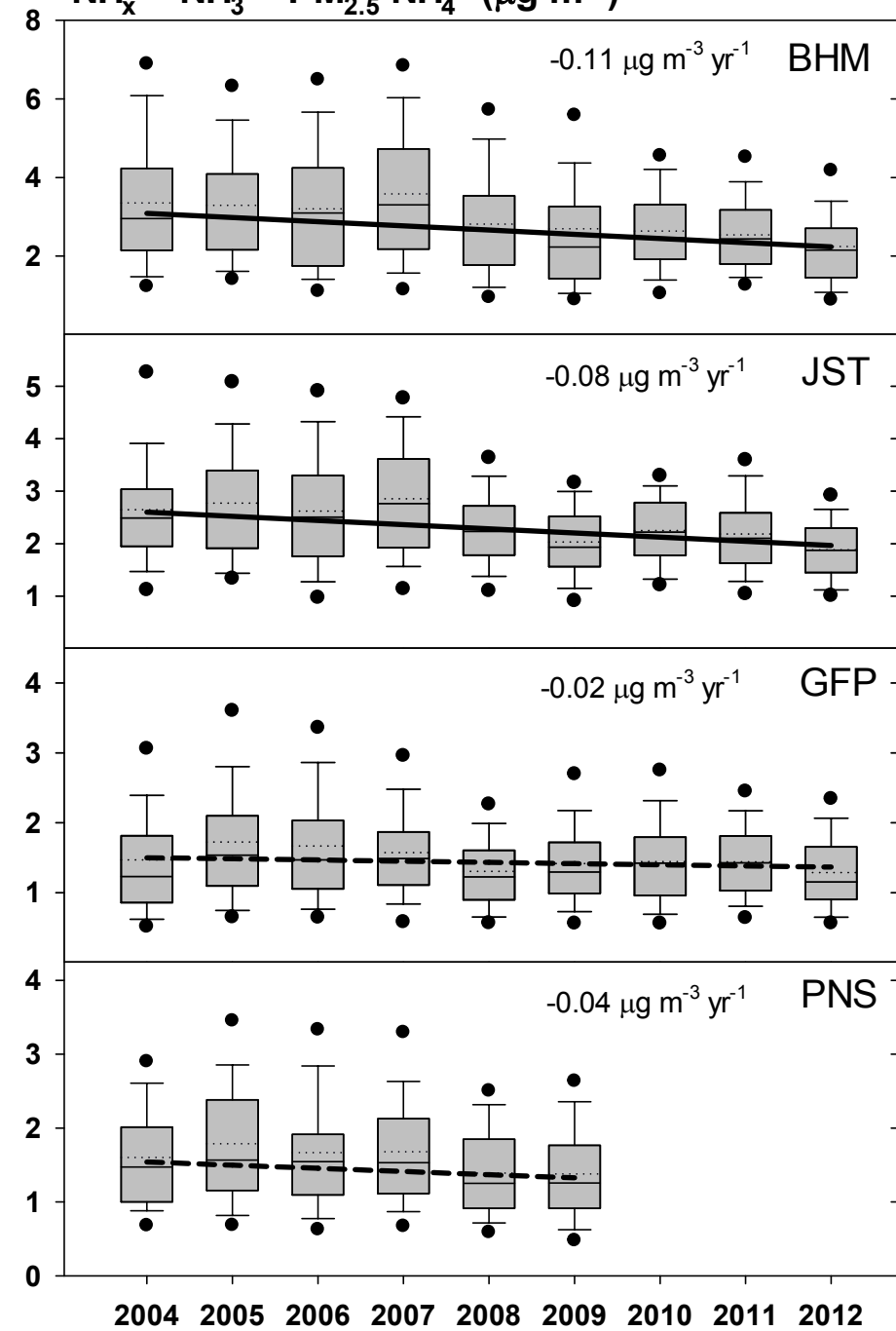
NH₃ SEARCH States
Xing et al. (2013)



NH₃ (ppbv)

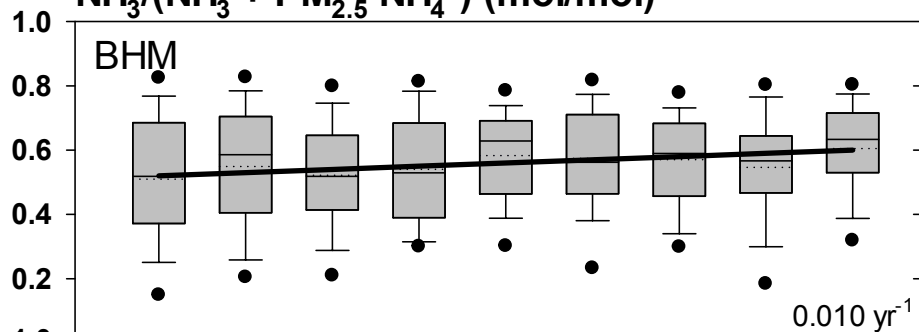


$\text{NH}_x = \text{NH}_3 + \text{PM}_{2.5} \text{NH}_4^+ (\mu\text{g m}^{-3})$

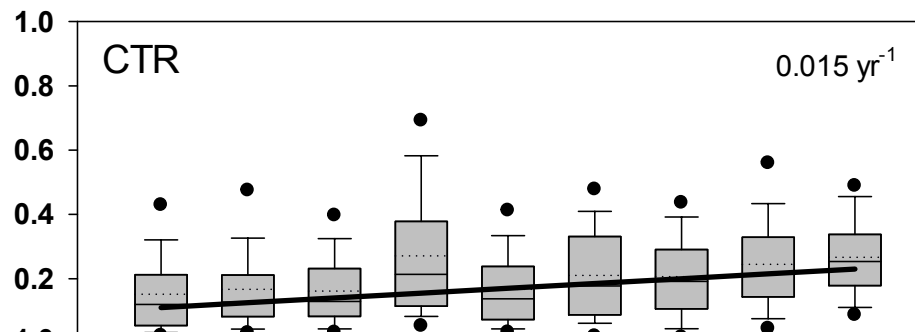


$\text{NH}_3/(\text{NH}_3 + \text{PM}_{2.5} \text{NH}_4^+) \text{ (mol/mol)}$

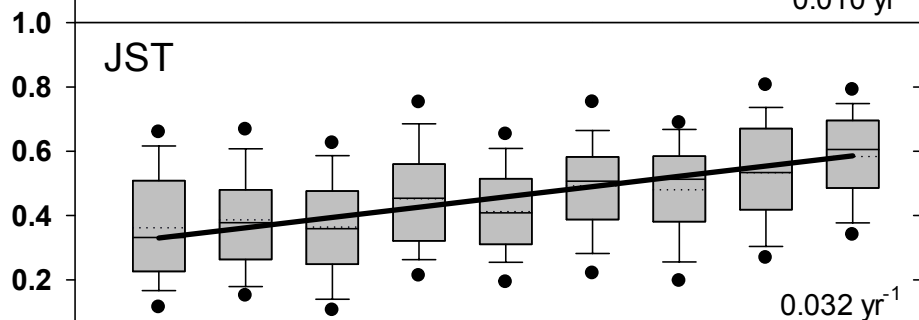
BHM



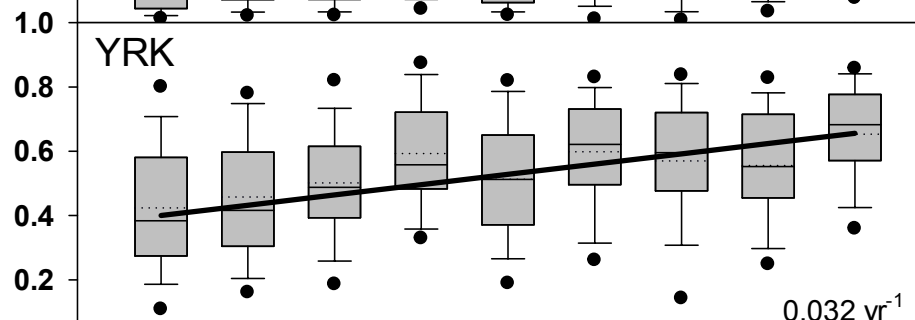
CTR



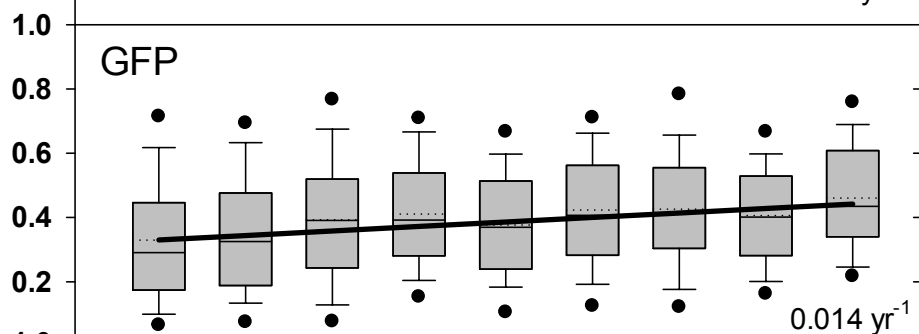
JST



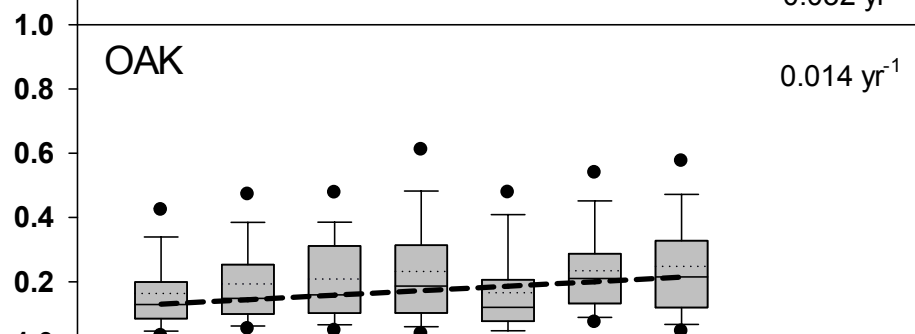
YRK



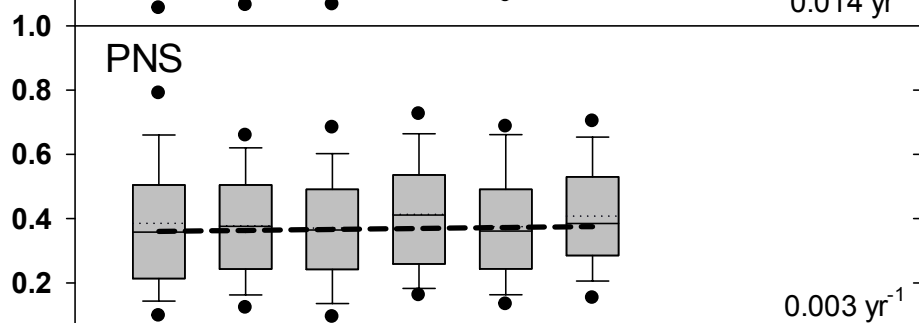
GFP



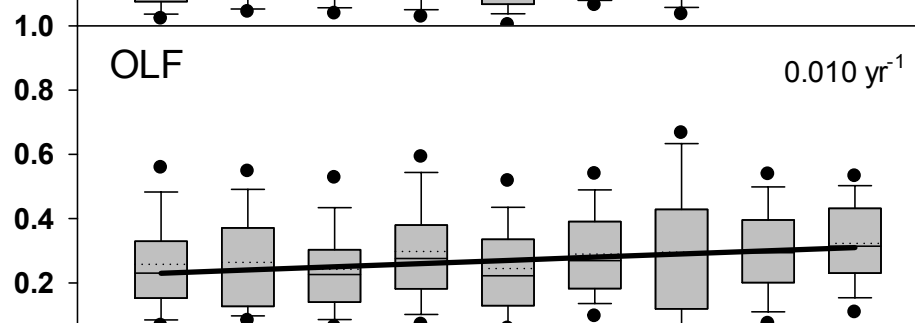
OAK



PNS



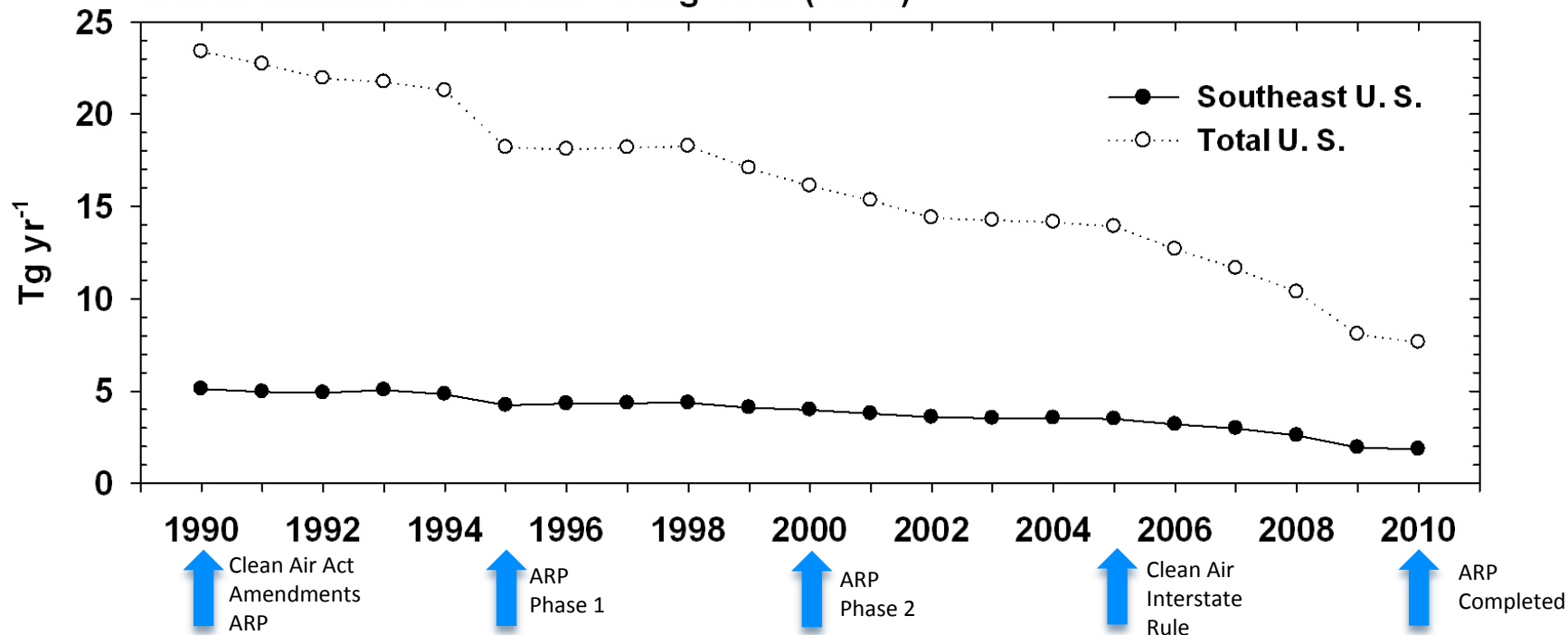
OLF



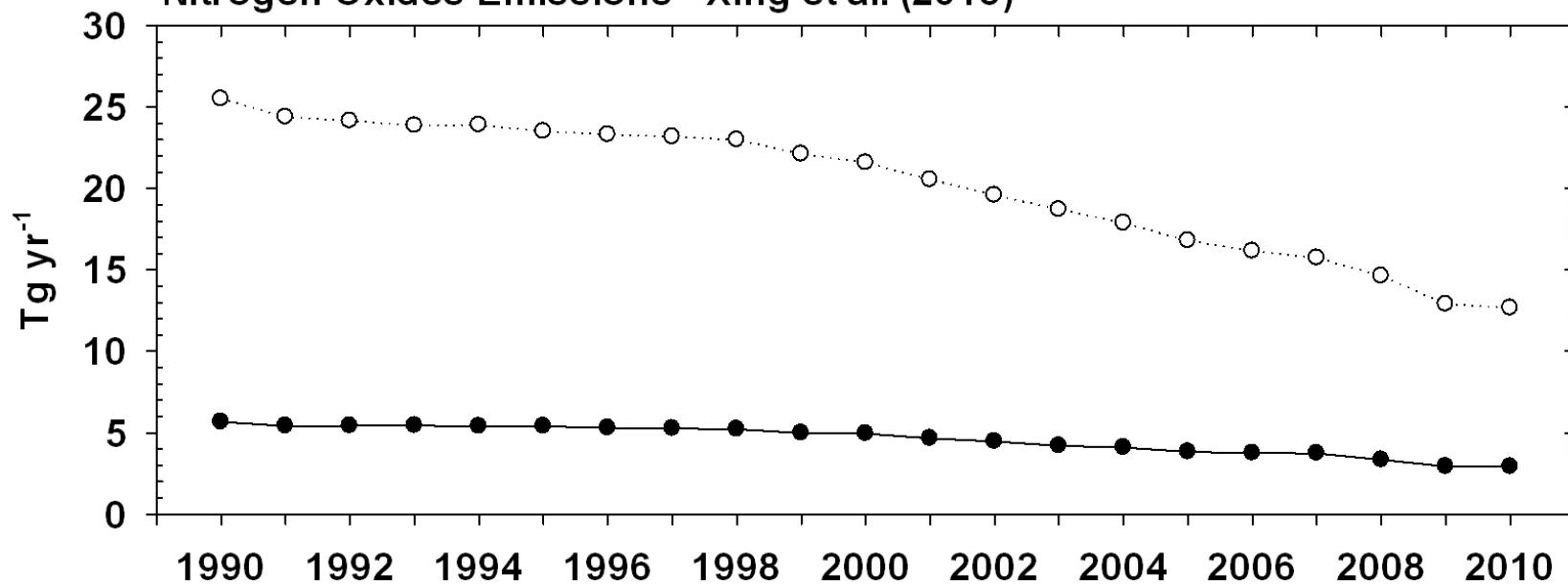
2004 2005 2006 2007 2008 2009 2010 2011 2012

2004 2005 2006 2007 2008 2009 2010 2011 2012

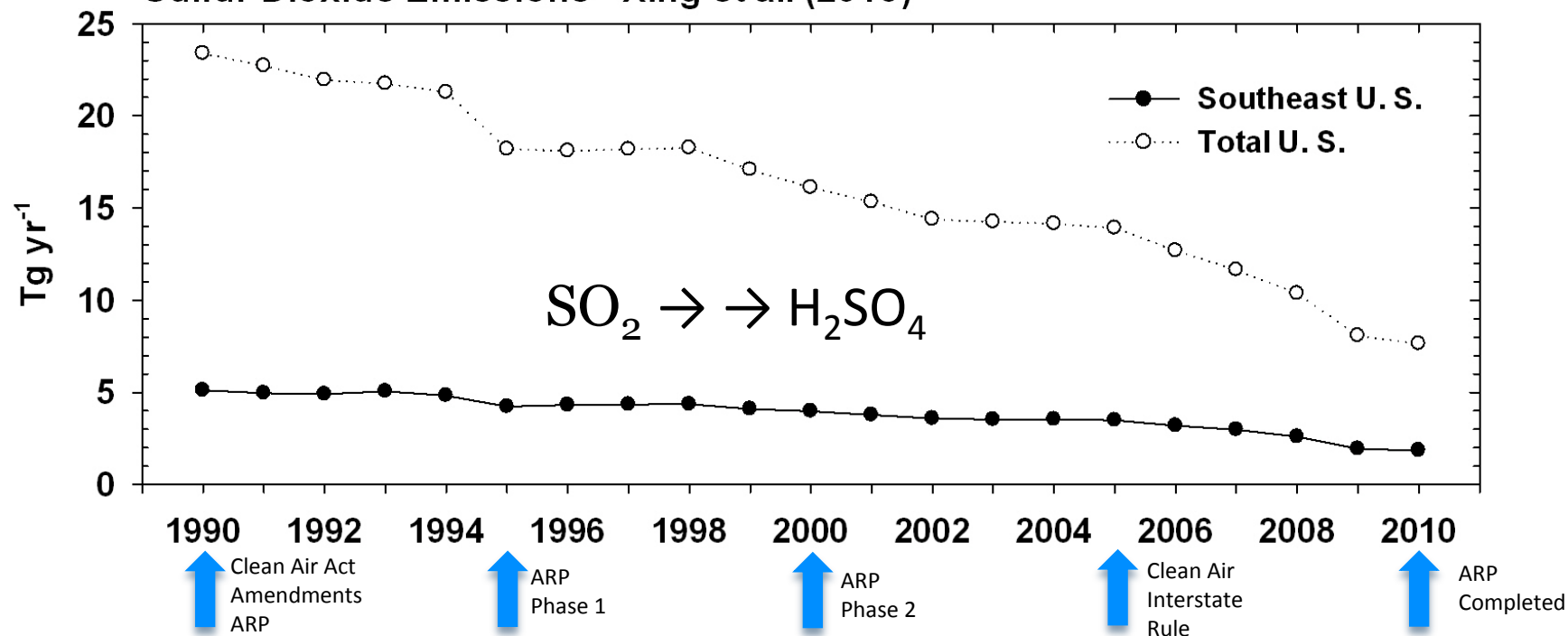
Sulfur Dioxide Emissions - Xing et al. (2013)



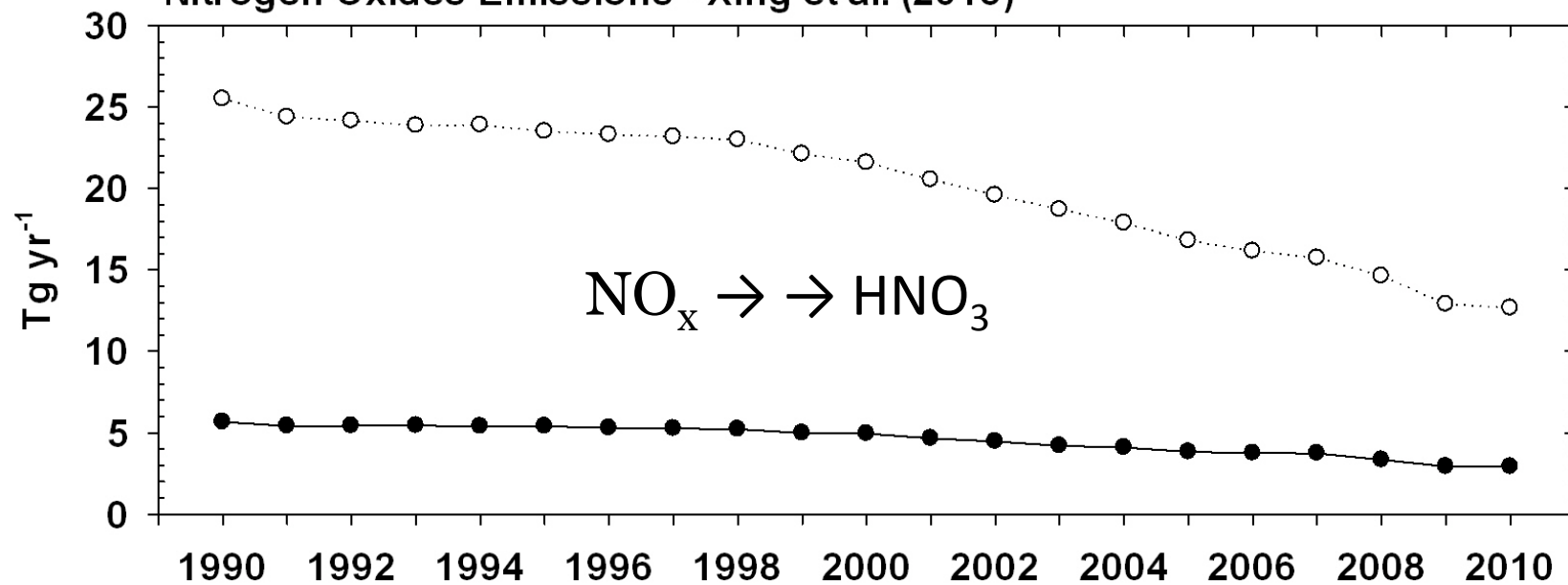
Nitrogen Oxides Emissions - Xing et al. (2013)



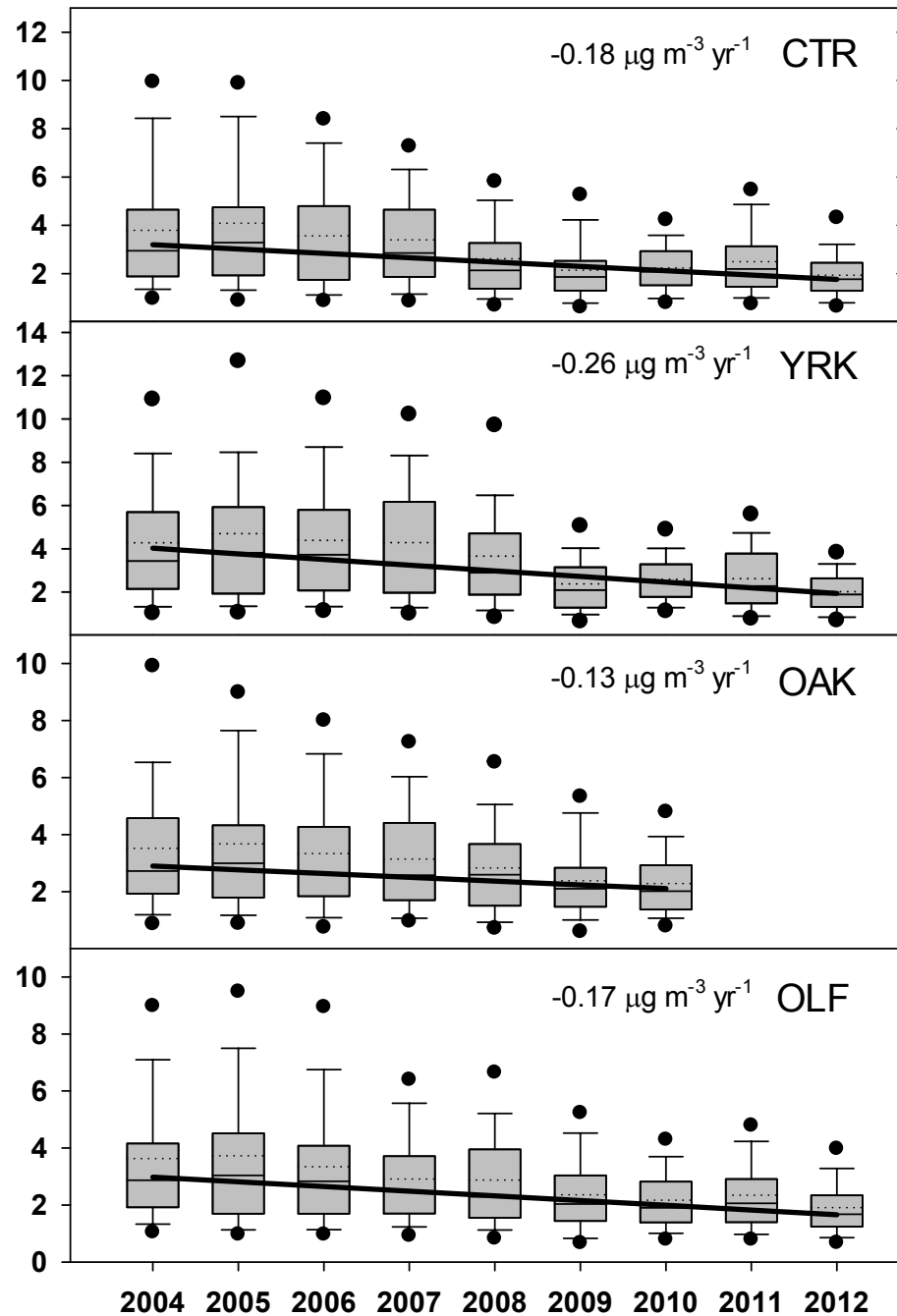
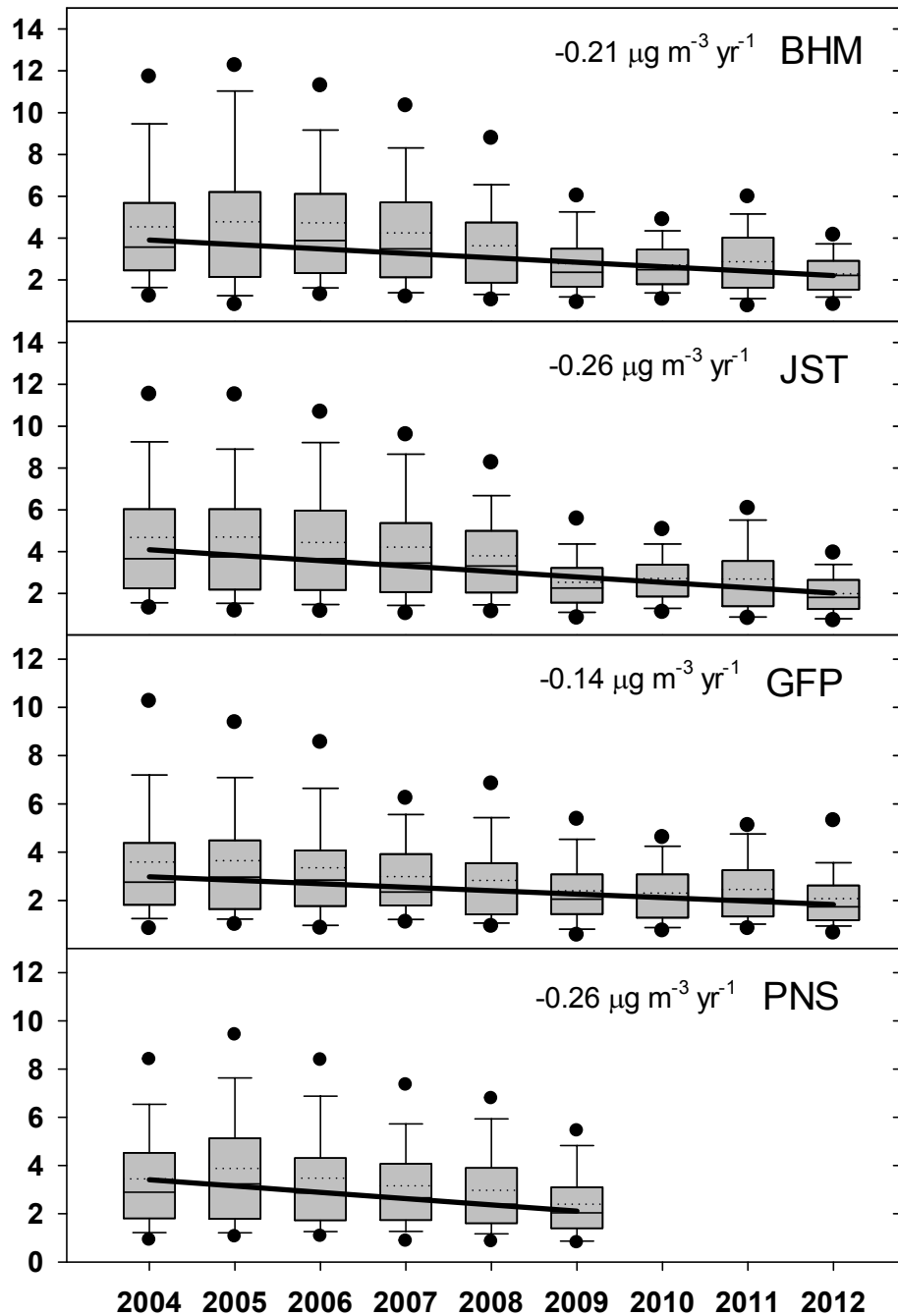
Sulfur Dioxide Emissions - Xing et al. (2013)



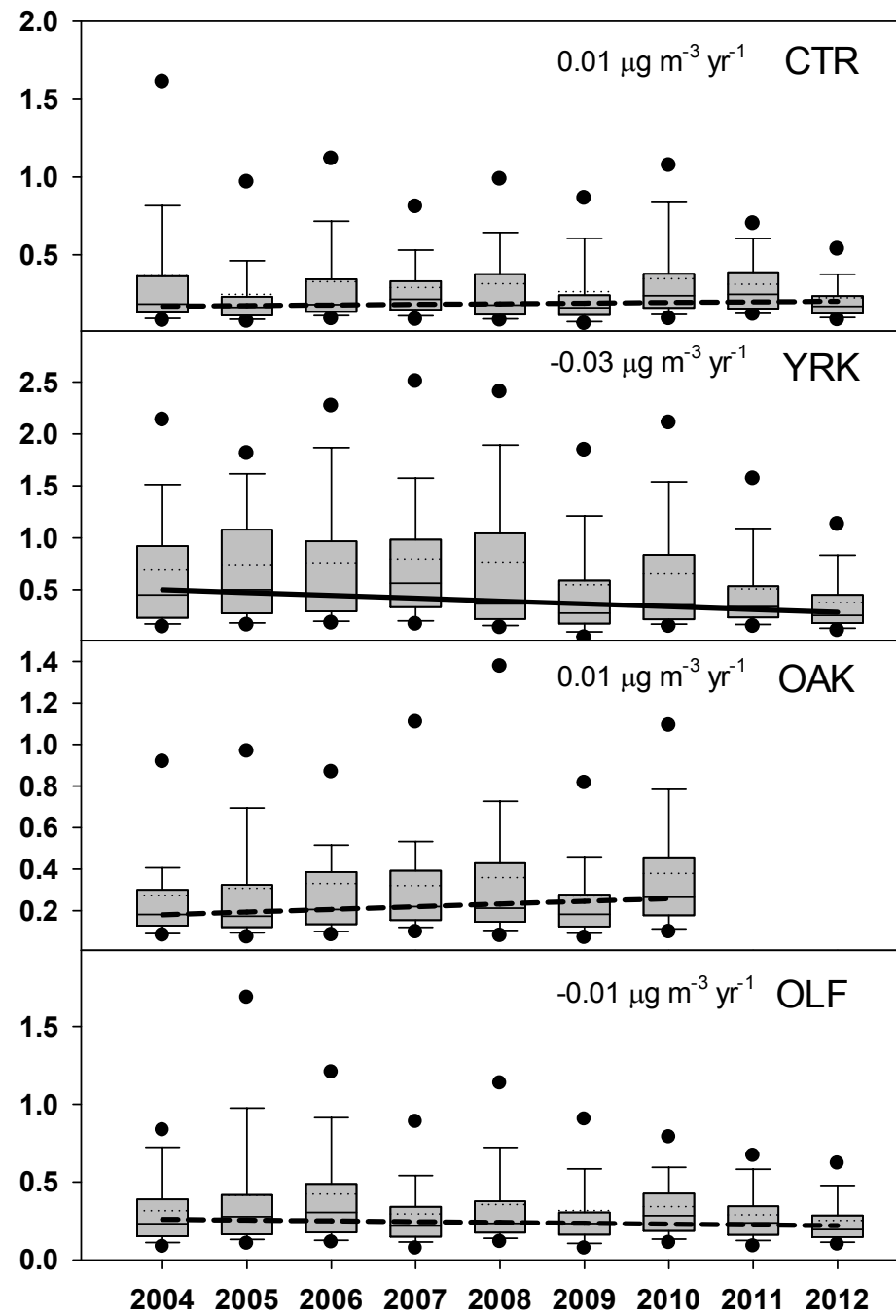
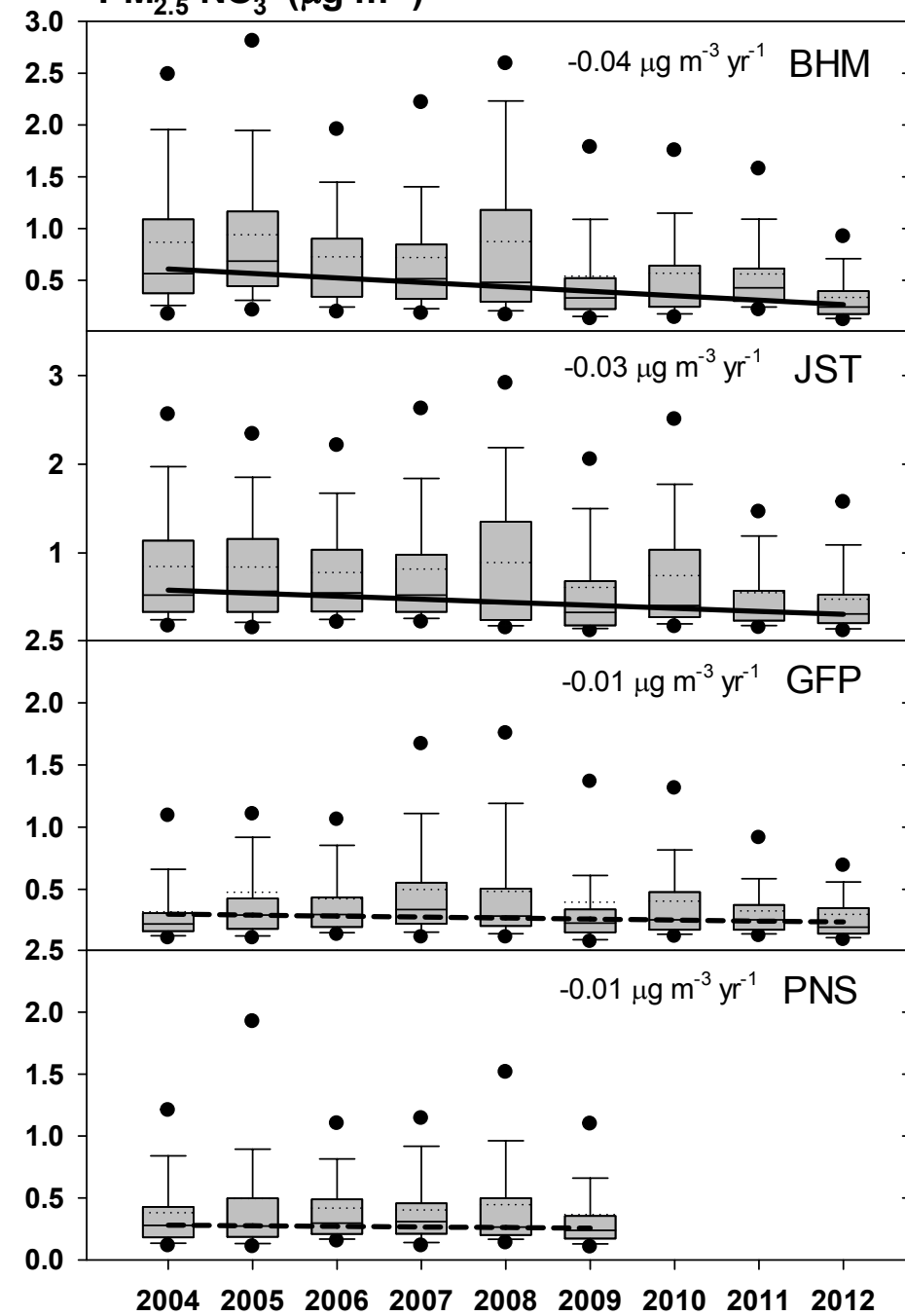
Nitrogen Oxides Emissions - Xing et al. (2013)



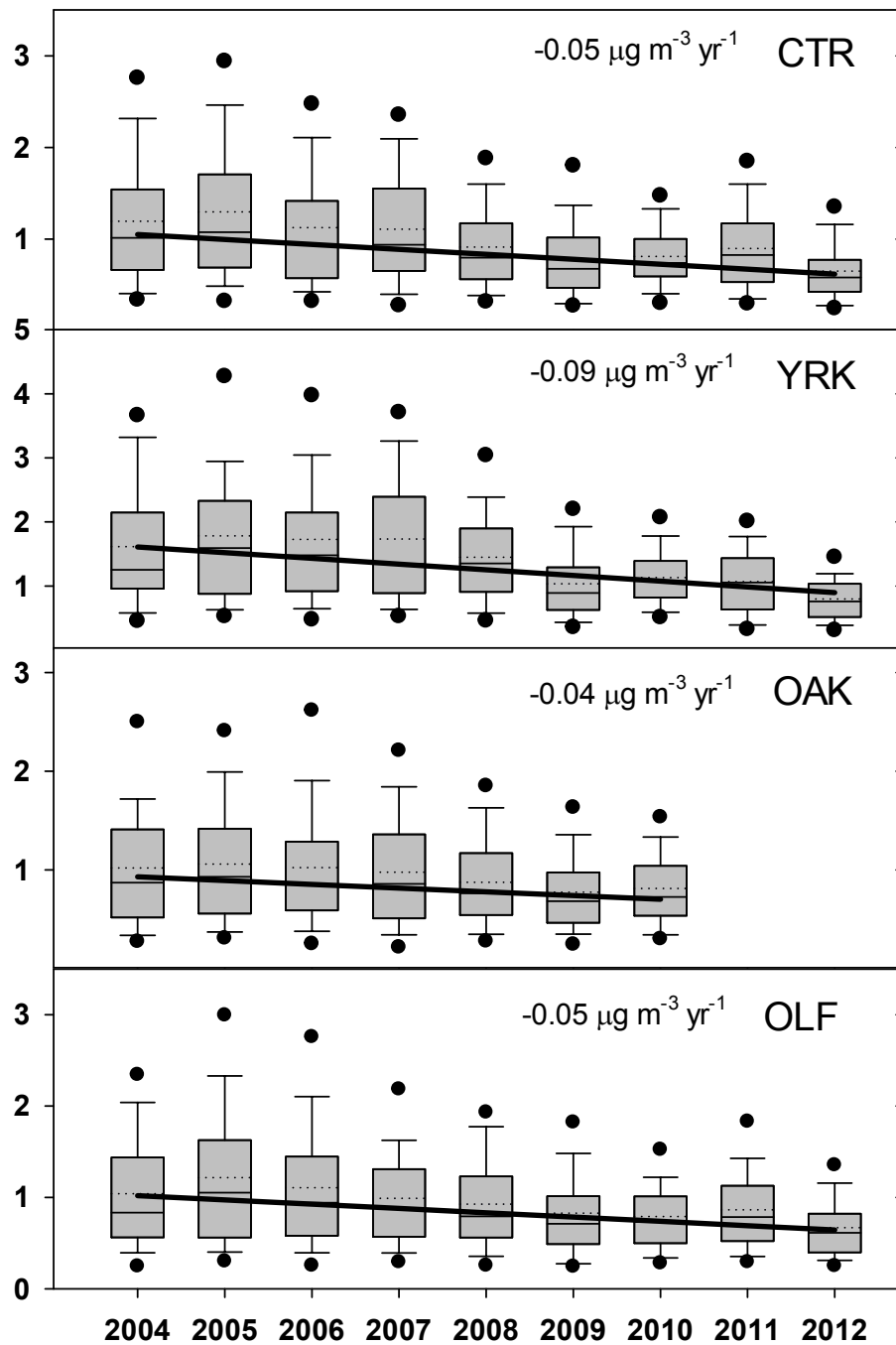
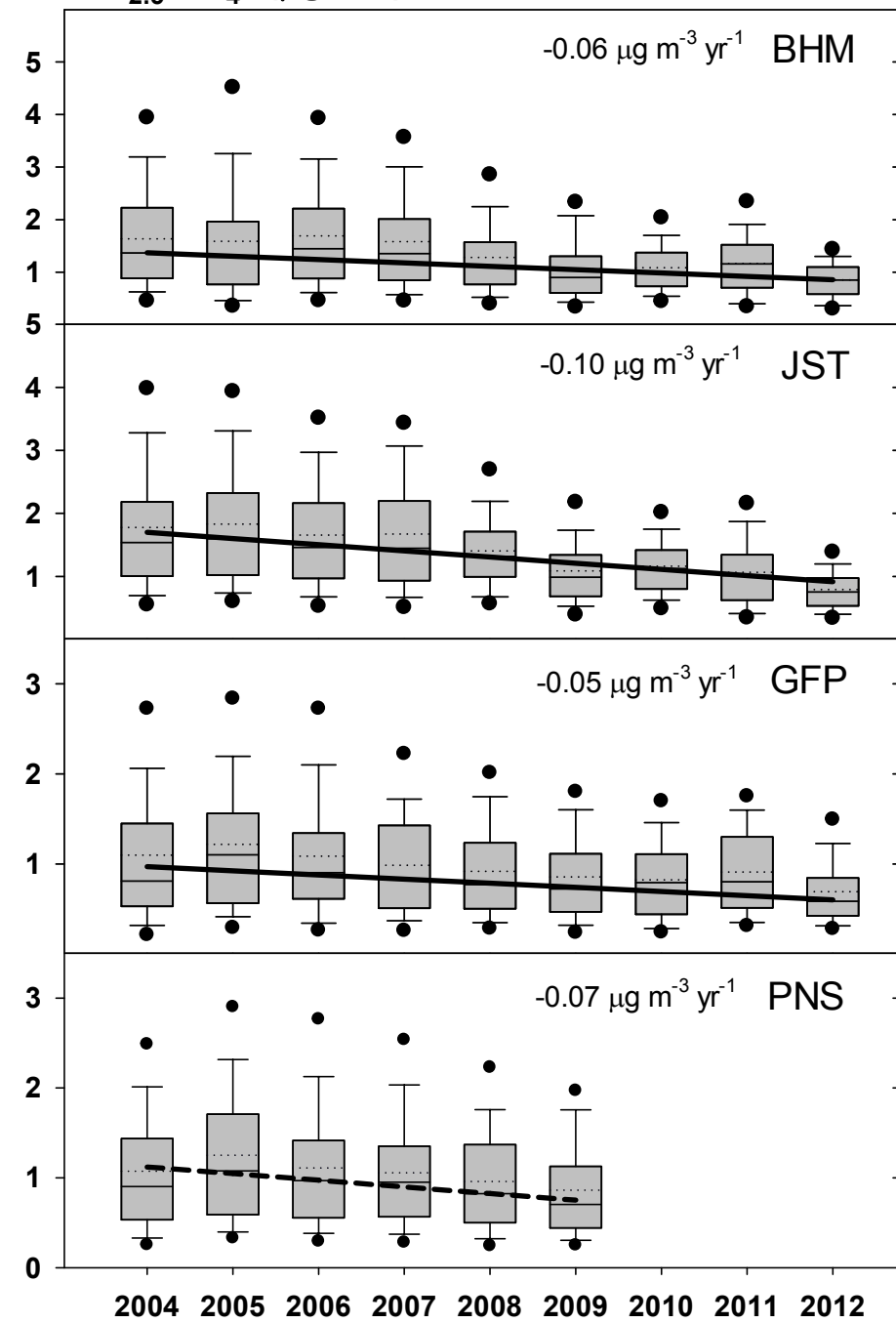
PM_{2.5} SO₄²⁻ (μg m⁻³)



PM_{2.5} NO₃⁻ (μg m⁻³)

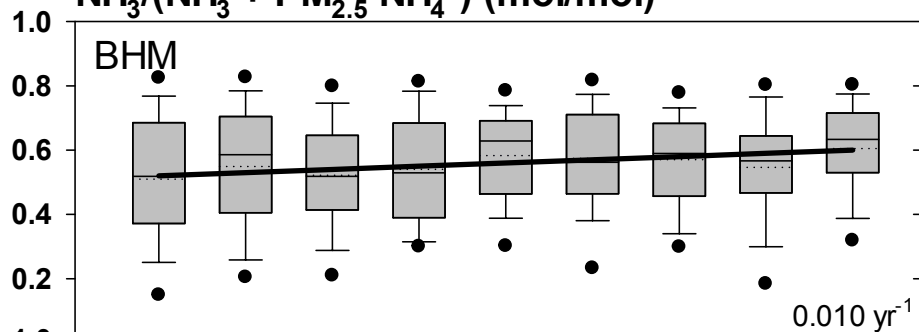


PM_{2.5} NH₄⁺ (μg m⁻³)

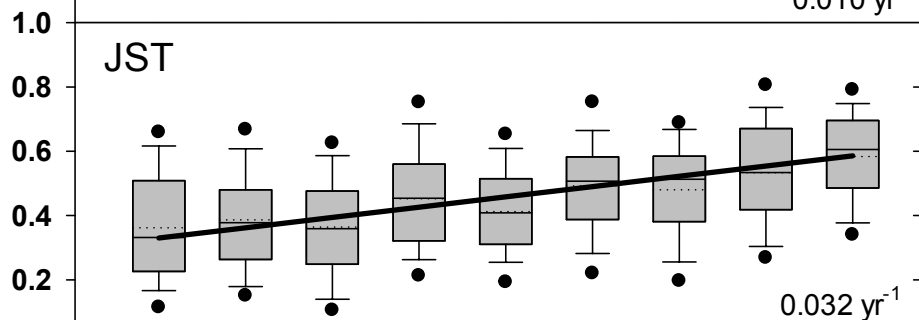


$\text{NH}_3/(\text{NH}_3 + \text{PM}_{2.5} \text{NH}_4^+) \text{ (mol/mol)}$

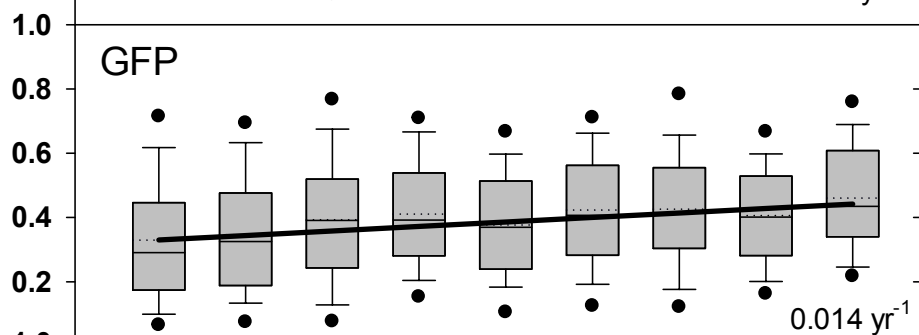
BHM



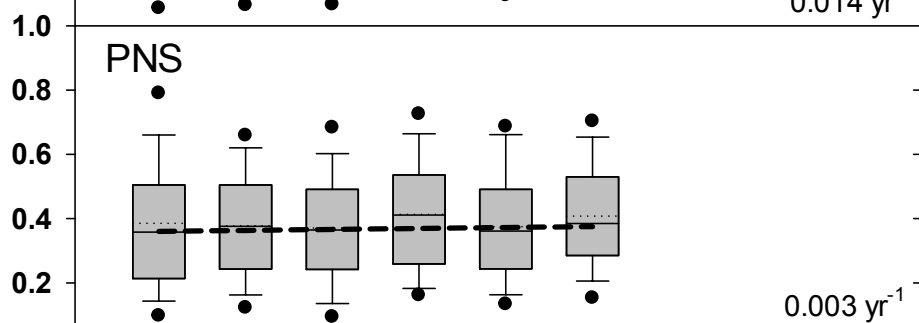
JST



GFP

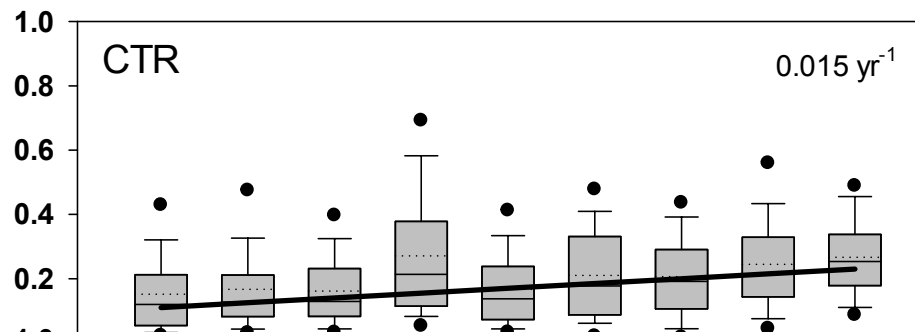


PNS

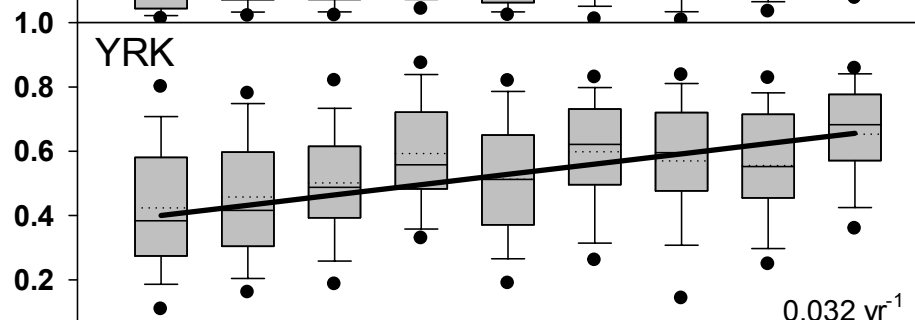


2004 2005 2006 2007 2008 2009 2010 2011 2012

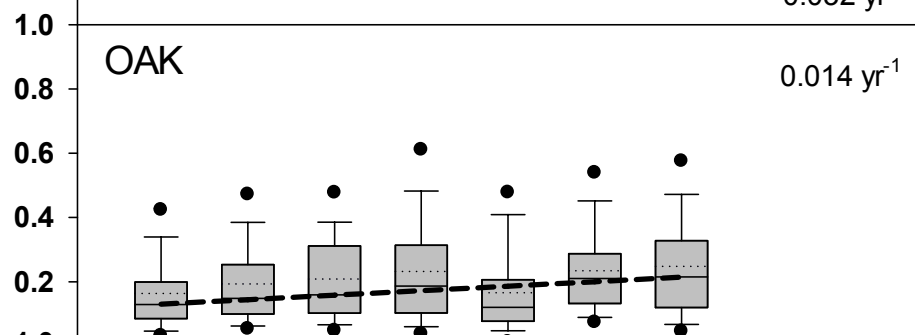
CTR



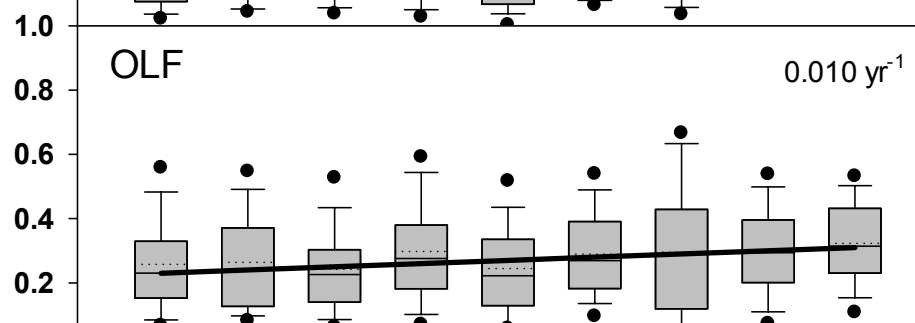
YRK



OAK



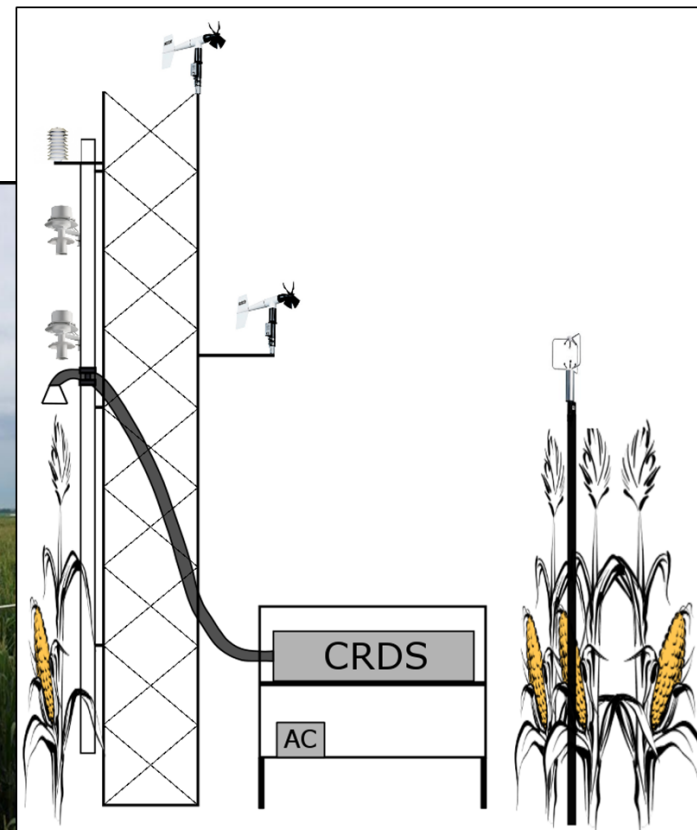
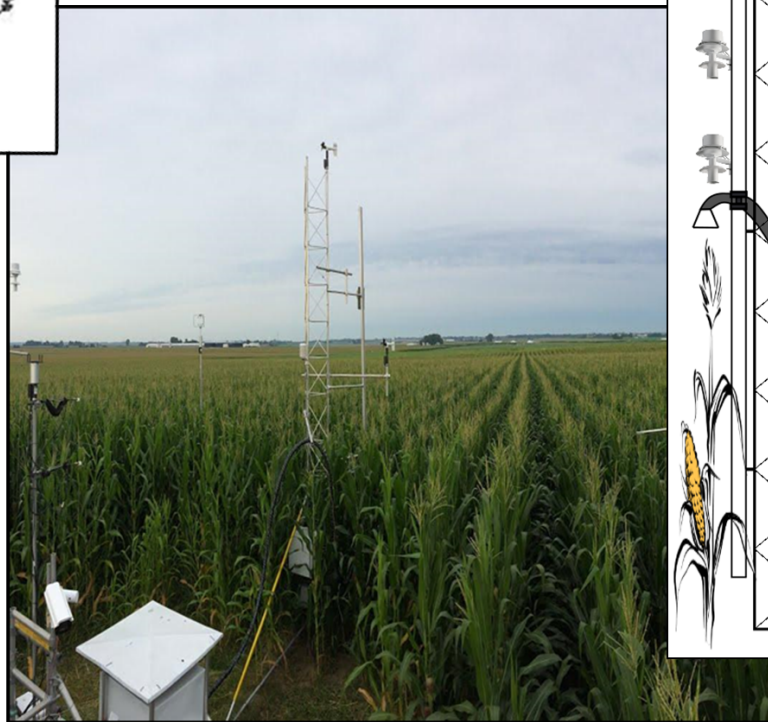
OLF



2004 2005 2006 2007 2008 2009 2010 2011 2012

2014 Illinois NH₃ Study - NSF

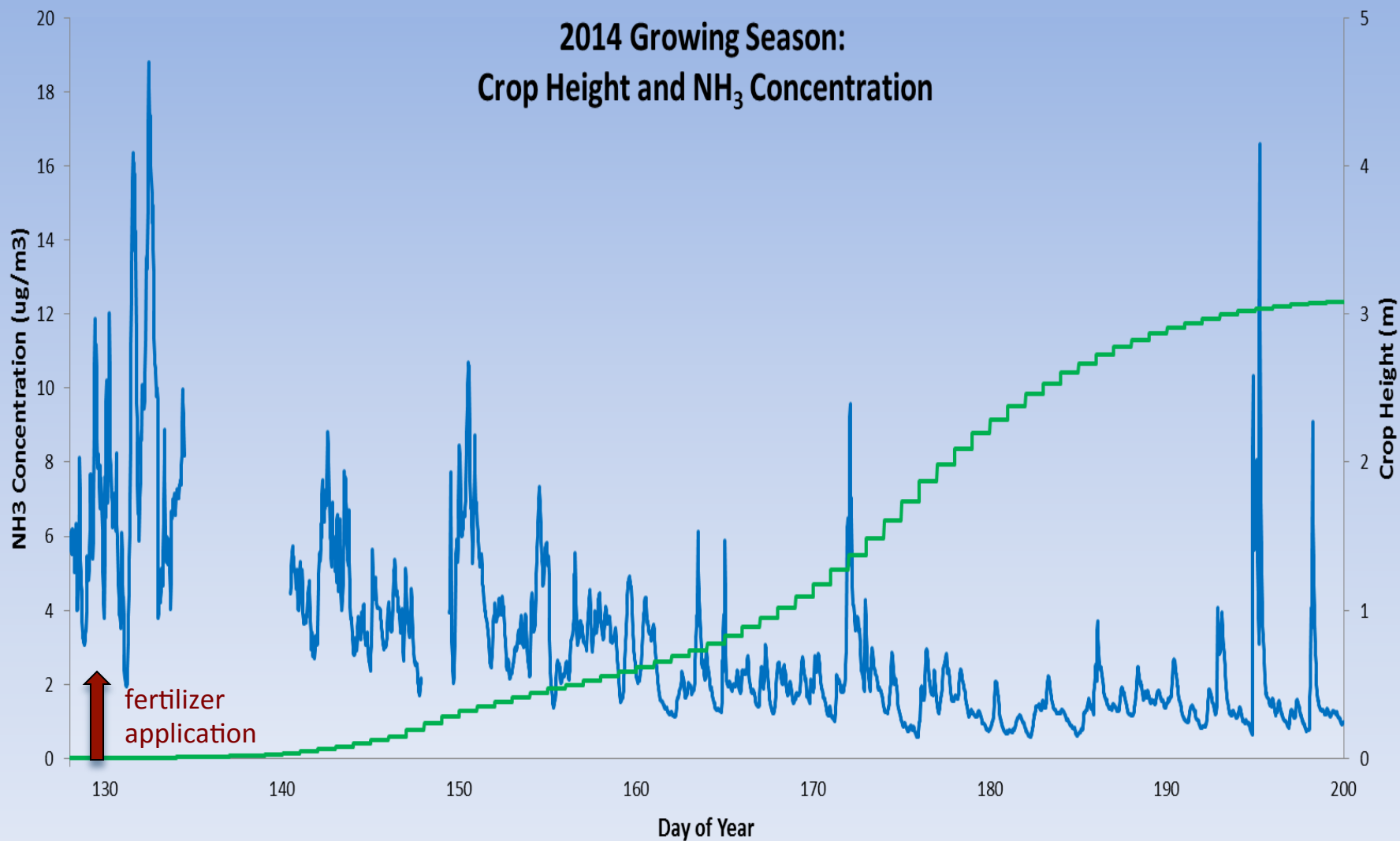
Dr. LaToya Myles (ATDD) and Dr. Sotiria Koloutsou-Vakakis (U. Illinois)

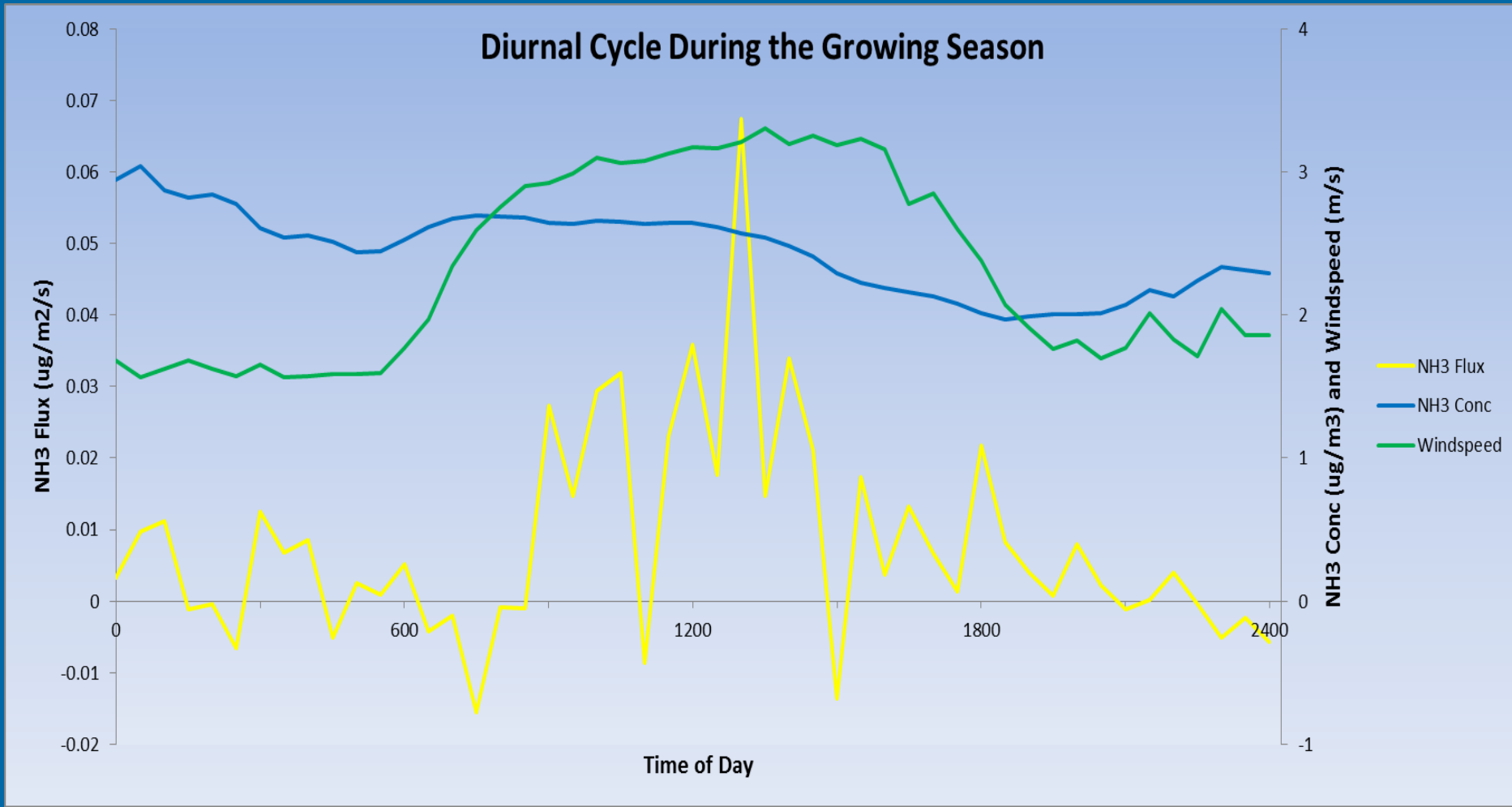


Ambient NH ₃ concentrations	Cavity Ring-Down Spectroscopy
Air temperature	Platinum Resistance Thermometers
Dewpoint	Humidity and Temperature Probe
Wind speed and direction	Propeller Anemometer
Pressure	Barometer

*Instruments in 200 m² Zea mays plot at UIUC Energy Biosciences Institute Farm in Urbana, IL (July 2014).
Photo Credit: A. Nelson*

2014 Growing Season: Crop Height and NH_3 Concentration







Atmospheric Chemistry and Canopy Exchange Simulation System for Ammonia (ACCESS-NH₃)

Final Governing Equation:

$$\frac{\partial \chi(z,t)}{\partial t} = \frac{\partial}{\partial z} \left(\rho(z,t) K_v(z,t) \frac{\partial \chi(z,t) / \rho(z,t)}{\partial z} \right) - v_c(z,t) (\chi(z,t) - \chi_c(z,t)) \cdot LAD(z)$$

Initial Condition:

$$\chi(z,t) = \chi_0(z) \quad @ t = 0$$

Boundary Conditions:

$$-\rho(0,t) K_v(0,t) \frac{\partial \chi(0,t) / \rho(0,t)}{\partial z} = -v_s(t) (\chi(0,t) - \chi_g(t)) \quad @ z = 0$$

$$\chi(H,t) = \chi_a(t) \quad @ z = H$$

where,

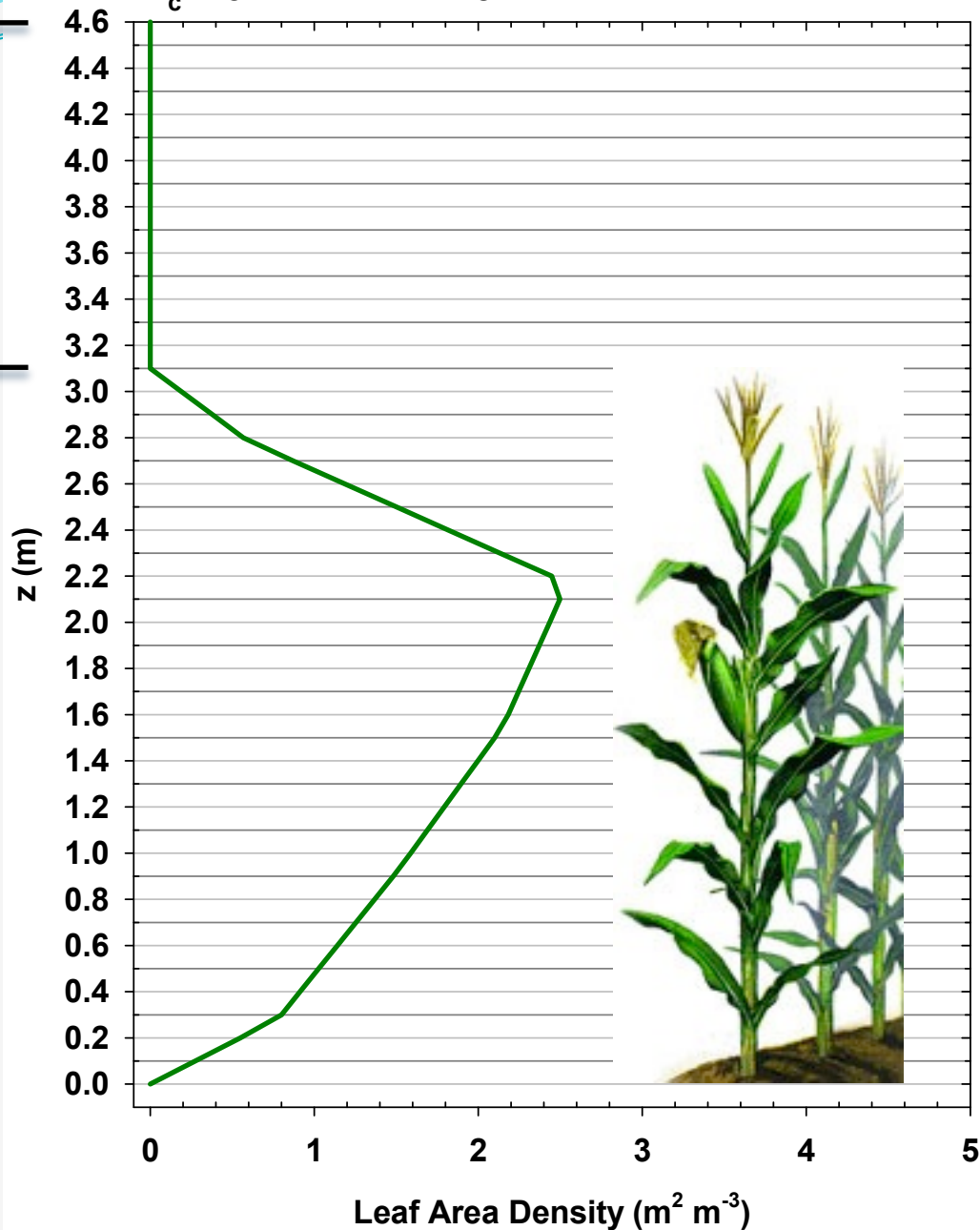
$\chi_g(t)$ = soil NH₃ compensation point

$\chi_a(t)$ = NH₃ concentration at $z = H$

Scaled - Ivanov et al. (1995)

$h_c = 3.1$ m $LAI = 4.5$

h_c



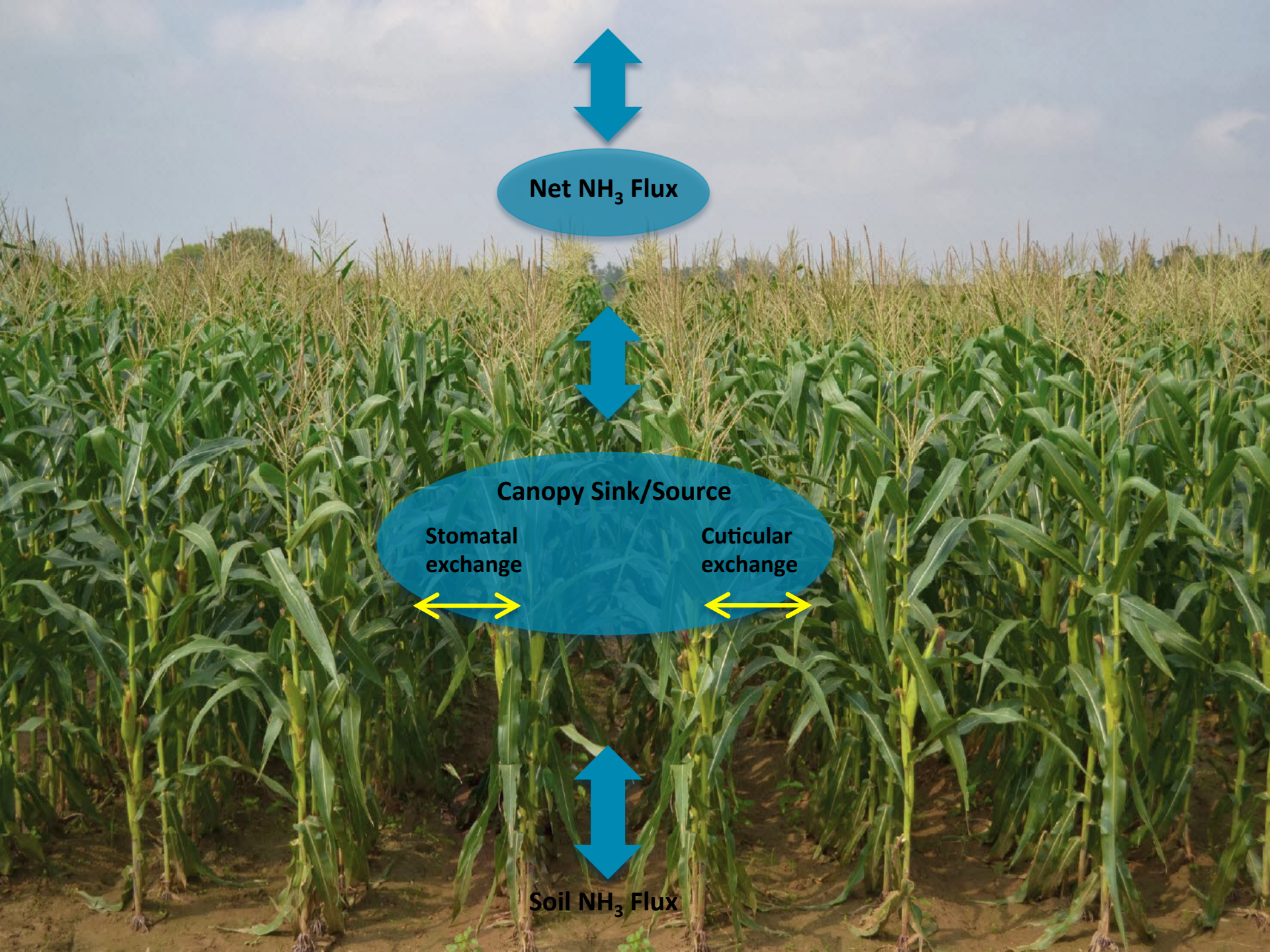
- 1-D column model
- Surface to 1.5 m above canopy top
- 46 vertical layers
- 0.1 m (10 cm) resolution throughout domain
- LAD scaled from data of Ivanov et al. (1995) for a maize canopy



Atmospheric Chemistry and Canopy Exchange Simulation System for Ammonia (ACCESS-NH3)

Input Variables

- Latitude/Longitude; Month, Day, Time
- Canopy morphology (canopy height, h_c ; leaf area density profile $LAD(z)$)
- Soil data (soil type; topsoil depth, d_s ; volumetric water content, θ)
- NH_3 Concentration @ $z = H$ ($H = h_c + 1.5 \text{ m} = 4.6 \text{ m}$)
- Air temperature @ 3.95 m, soil temperature, pressure @ 0.8 m, relative humidity @ 3.95 m
- Mean wind speed, $\bar{u}$, shortwave radiation, and PPFD @ 3.95 m
- Stomatal Emission Potential ... $\Gamma_s = [NH_4^+]_s / [H^+]_s$
- Soil Emission Potential ... $\Gamma_g = [NH_4^+]_g / [H^+]_g$



Net NH₃ Flux

Canopy Sink/Source

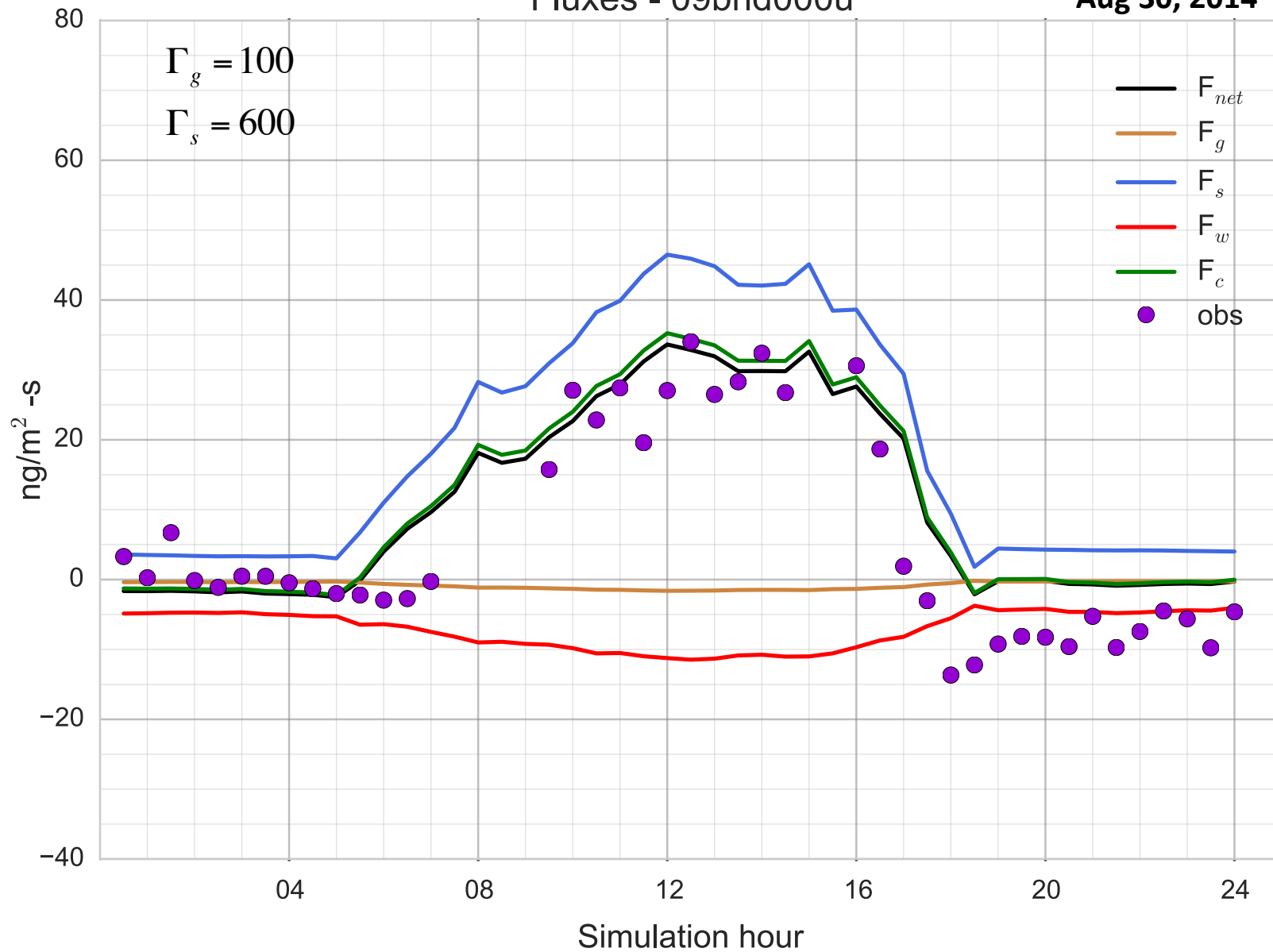
**Stomatal
exchange**

**Cuticular
exchange**

Soil NH₃ Flux

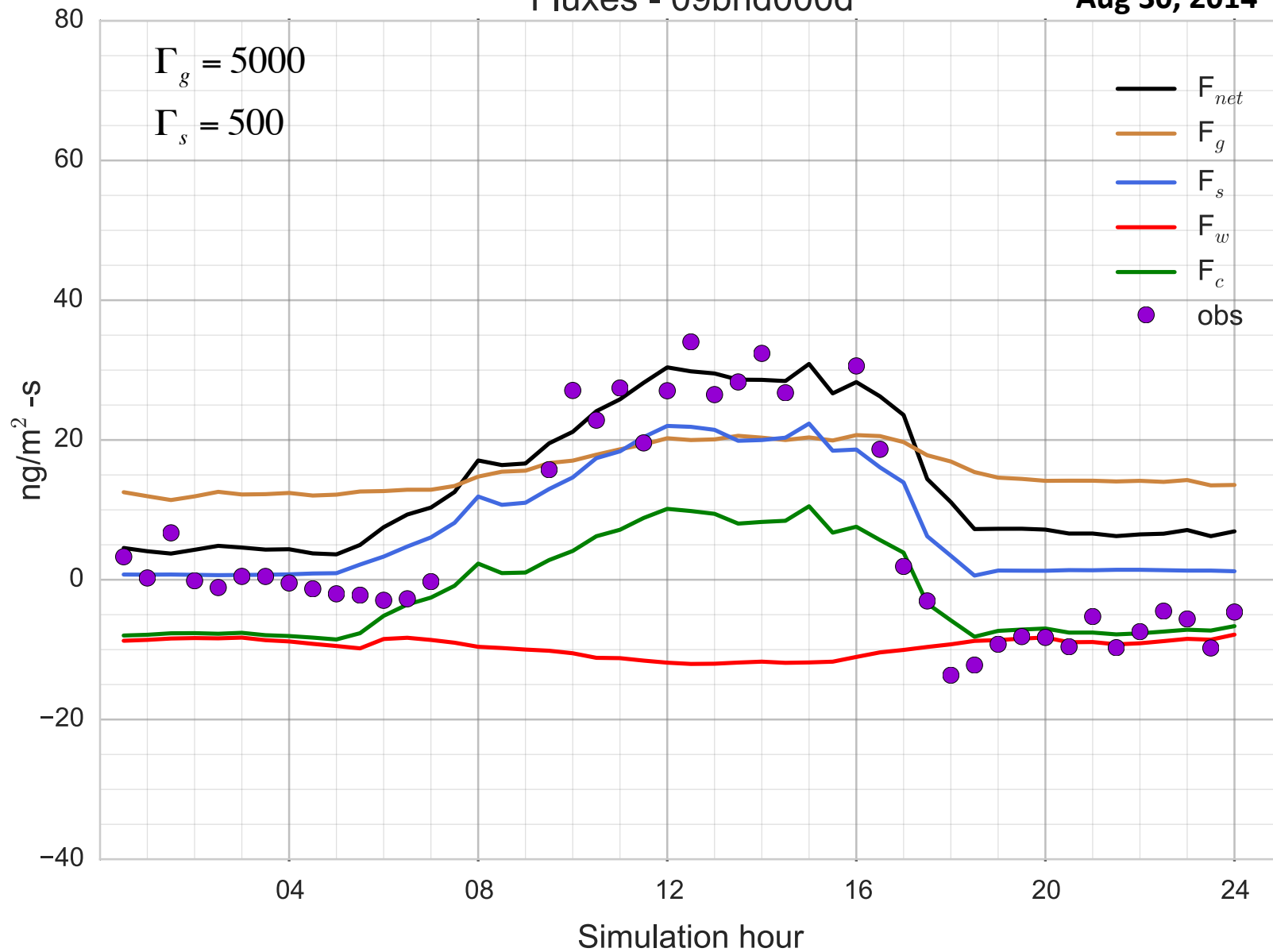
Fluxes - 09bnd000u

Aug 30, 2014



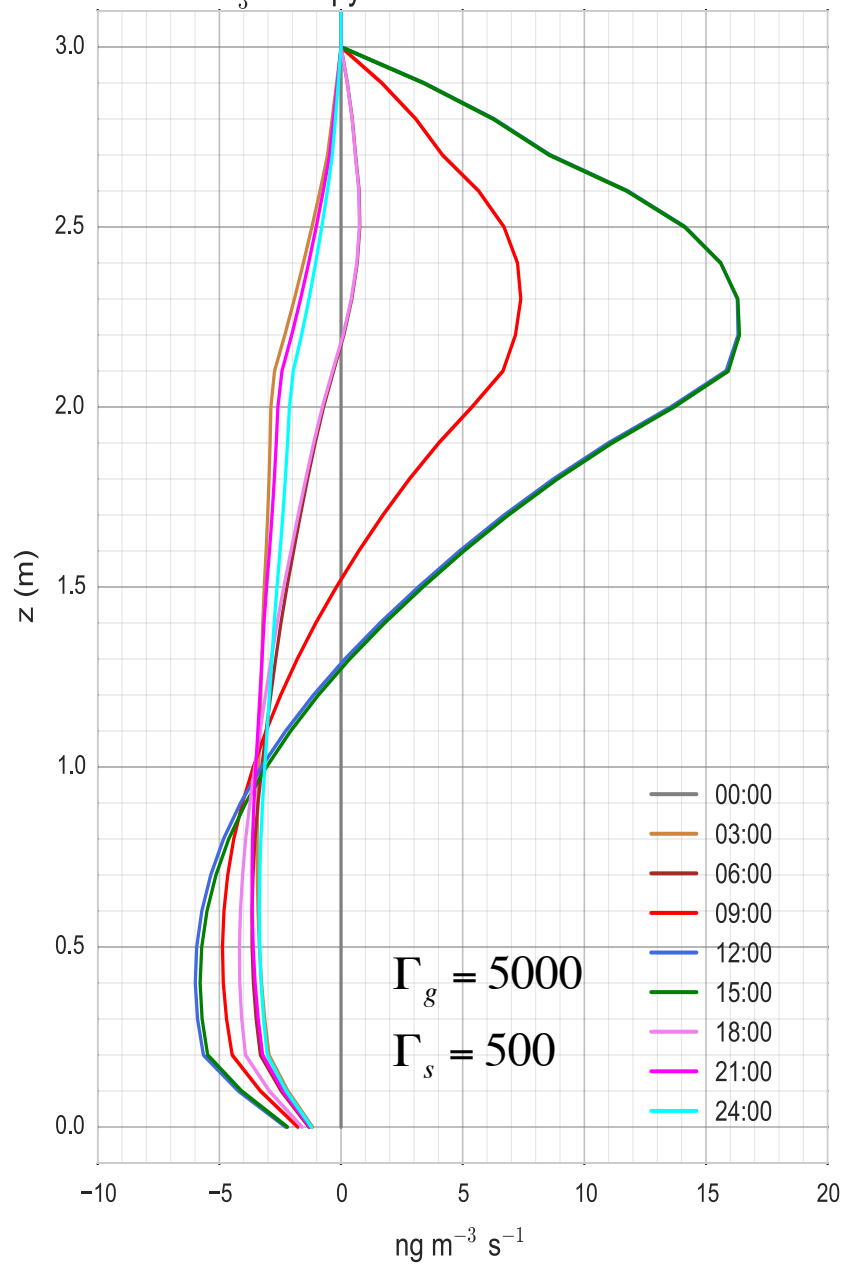
Fluxes - 09bnd000d

Aug 30, 2014

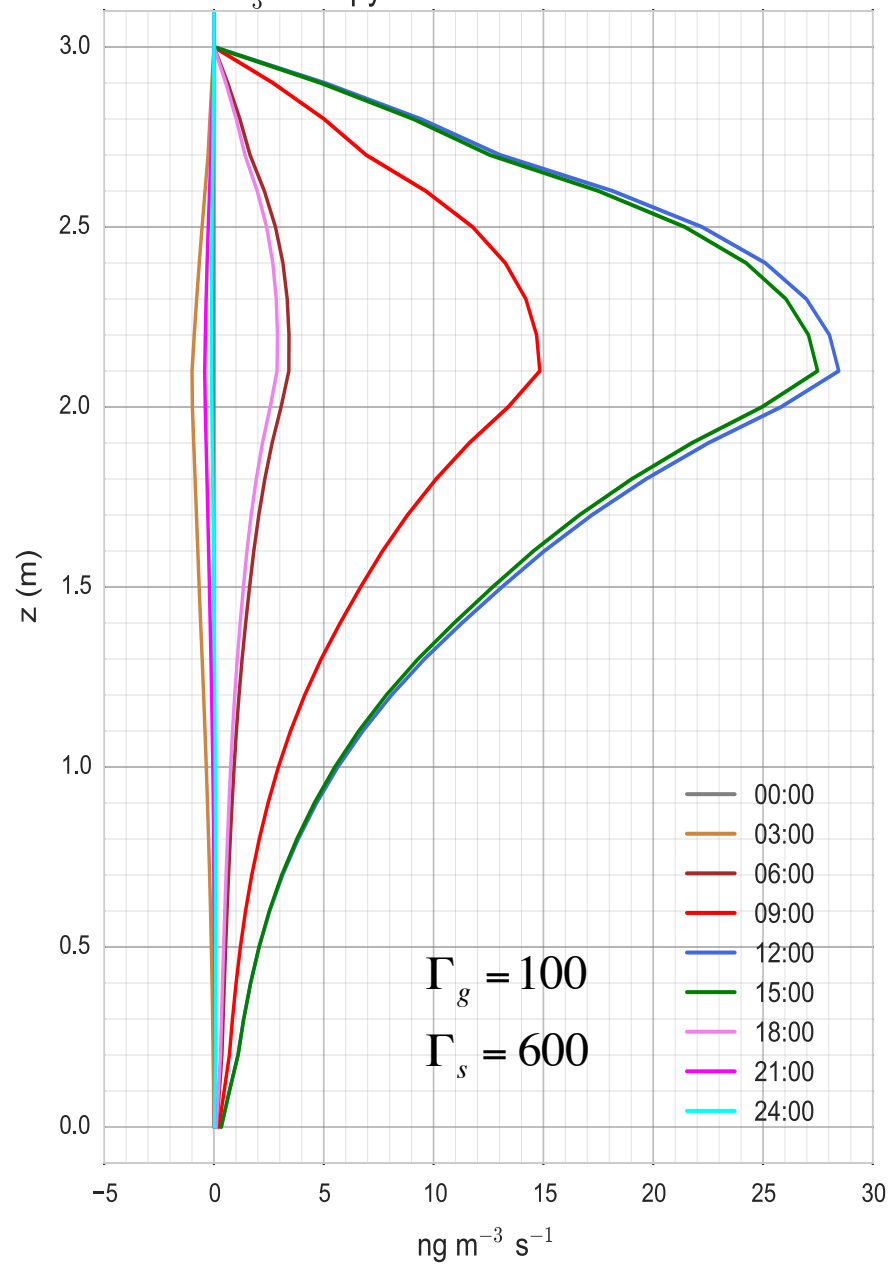


Aug 30, 2014

NH₃ Canopy Source Profile - 09bnd000d



NH₃ Canopy Source Profile - 09bnd000u

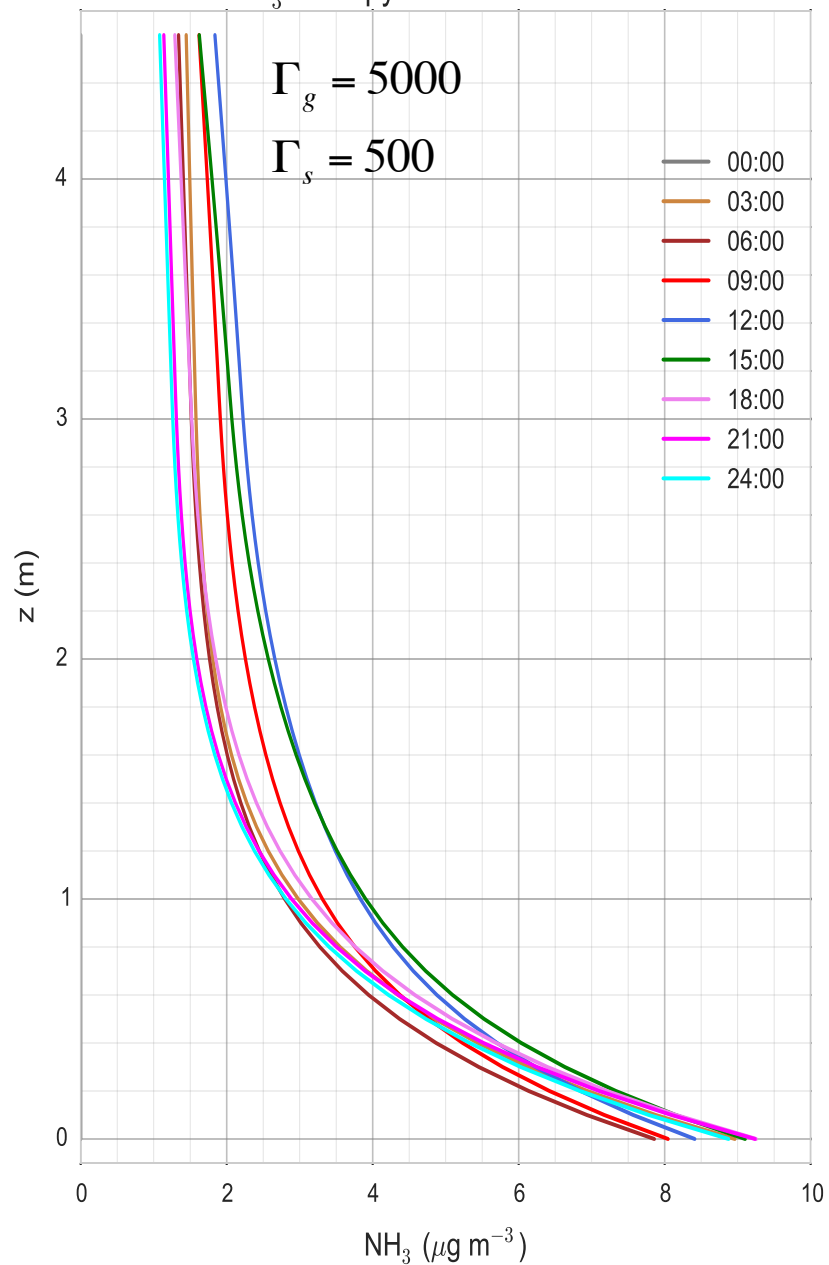


Aug 30, 2014

NH₃ Canopy Profile - 09bnd000d

$$\Gamma_g = 5000$$

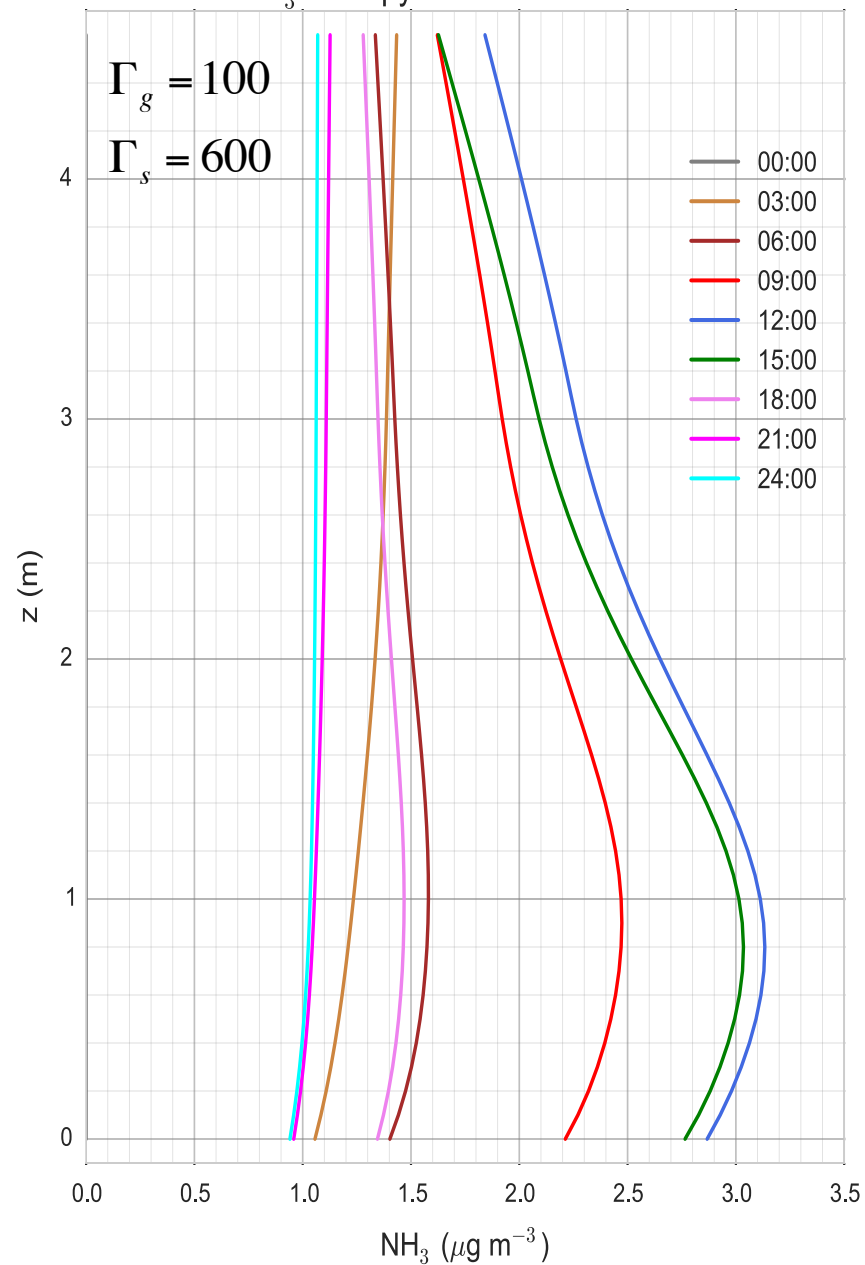
$$\Gamma_s = 500$$



NH₃ Canopy Profile - 09bnd000u

$$\Gamma_g = 100$$

$$\Gamma_s = 600$$





Future Directions

Measurements

- ✓ Intercomparisons between CRDS and other laser-based techniques, e.g. open path tunable diode laser (OPTDL), tunable diode laser absorption spectroscopy (TDLAS)
- ✓ Field measurements of fluxes in more complex ecosystems, including coastal marshes, where nutrient enrichment can affect vegetation and carbon exchange
- ✓ Field measurements of concentrations downwind from prescribed burns and/or wildfires (contribution to NOAA biennial study: FIREX)

Modeling

- ✓ Continued use of ACCESS-NH3 (and other NH_3 flux models) to better understand environmental controls of NH_3 fluxes from/to agricultural fields and coastal marshes (limited resources!).
- ✓ Evaluation of NH_3 emissions used in 3-D air quality models (esp. NAQFC) using AMoN and satellite data.



Research Needs

- ✓ U.S. ammonia emissions inventory remains highly uncertain.
 - Lack of information about agricultural emissions from various crops in different locations.
 - Lack of understanding about processes that drive NH_x exchange with soil, vegetation, and surface waters under different environmental conditions.
 - Lack of long-term measurements with adequate spatial and temporal resolution.
- ✓ More robust continuous measurement techniques for field applications.
- ✓ Better algorithms for simulation of bi-directional exchange within 3-D air quality models.



Thank you!

Questions?