United States Environmental Protection Agency

# Measurement and modeling of the contribution of ammonia to total nitrogen deposition from canopy to regional scale

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# Motivation

- As the most abundant reduced nitrogen compound in the atmosphere, ammonia ($NH_3$) plays an important role in aerosol formation and nitrogen deposition.
- The expansion of critical loads research has motivated efforts to develop quantitative speciated budgets of atmospheric nitrogen deposition.
- Relative to oxidized nitrogen, which is subject to regulatory control, much less is known regarding the contribution of $NH_3$ to the total pool of reactive nitrogen in the atmosphere and therefore in atmospheric deposition.
- While spatial and temporal patterns of $NH_4^+$ wet deposition across the U.S. are relatively well characterized, the contribution of $NH_3$ dry deposition to total nitrogen deposition is much less certain.
- This presentation explores the state-of-the-science of $NH_3$ dry deposition and the role of $NH_3$ in atmospheric nitrogen deposition in the United States.

# Outline

- Ammonia air-surface exchange processes
- Methods for determining ammonia air-surface fluxes
- Methods for constructing total N deposition budgets
- Case studies examining the contribution of $NH_3$ to total N deposition
- Recommendations for monitoring and process oriented research needed to improve site to regional scale estimates of $NH_3$ deposition

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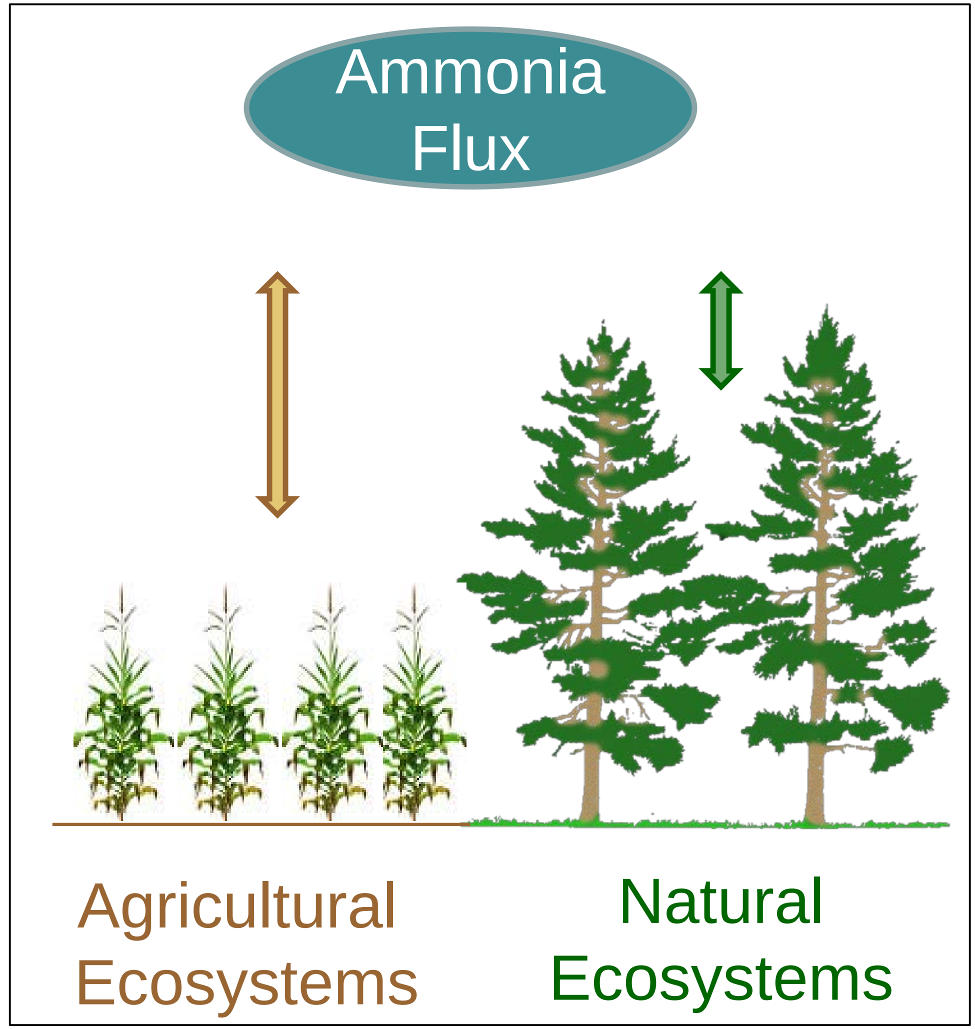
Ammonia may be emitted from or deposited to vegetation, soil, and water, depending on the ratio of the atmospheric $NH_3$ concentration to the “compensation point” of the underlying surface.

Ammonia air-surface exchange processes are “bi-directional”.

The compensation point ($\chi$) is governed by the nitrogen status and acidity of the exchange surface.

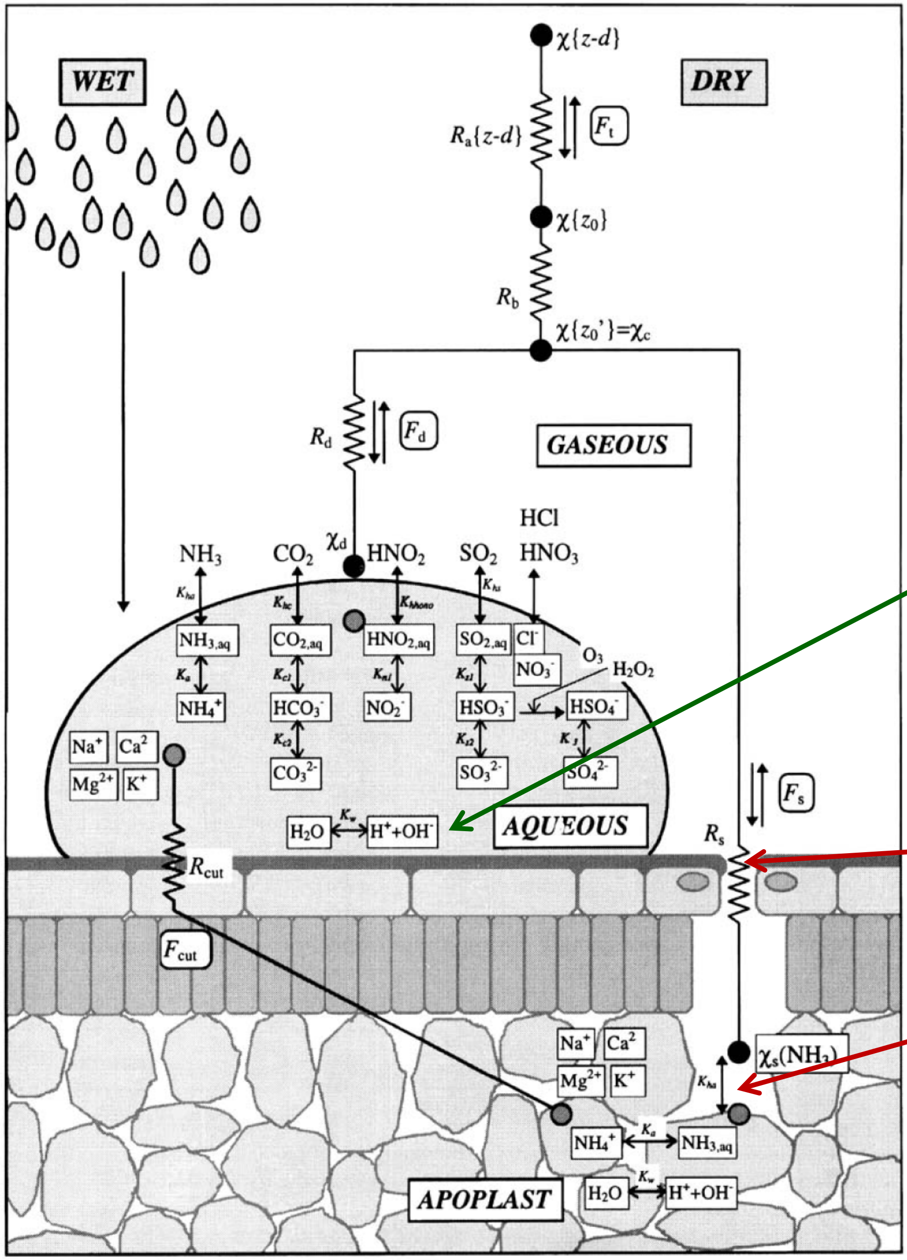



Compensation point

$$\chi = \frac{161500}{T} \exp\left(-\frac{10380}{T}\right) \frac{[NH_4^+]}{[H^+]}$$

Emission potential → Soil/litter; Leaf apoplast; Leaf surface water

# Schematic of leaf $NH_3$ exchange processes (Flechard et al., 1999)

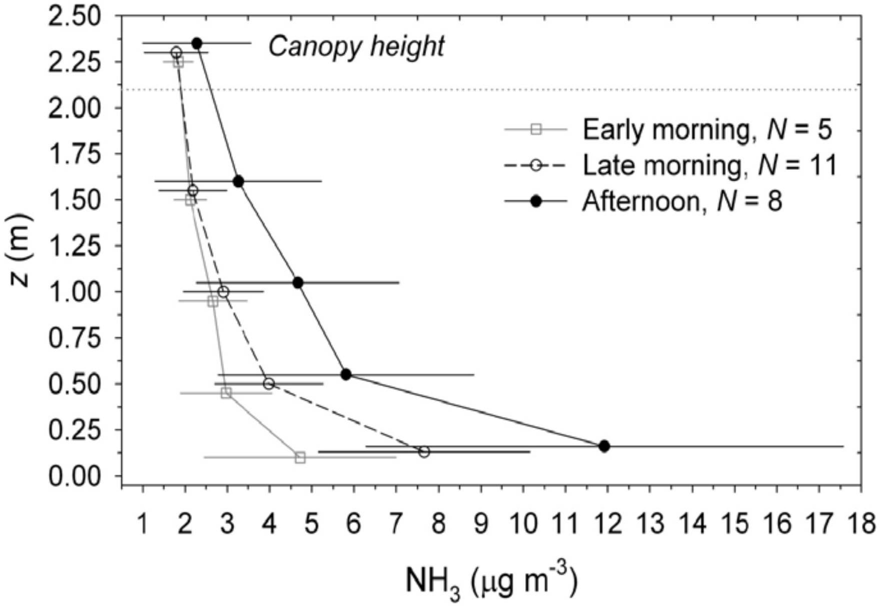


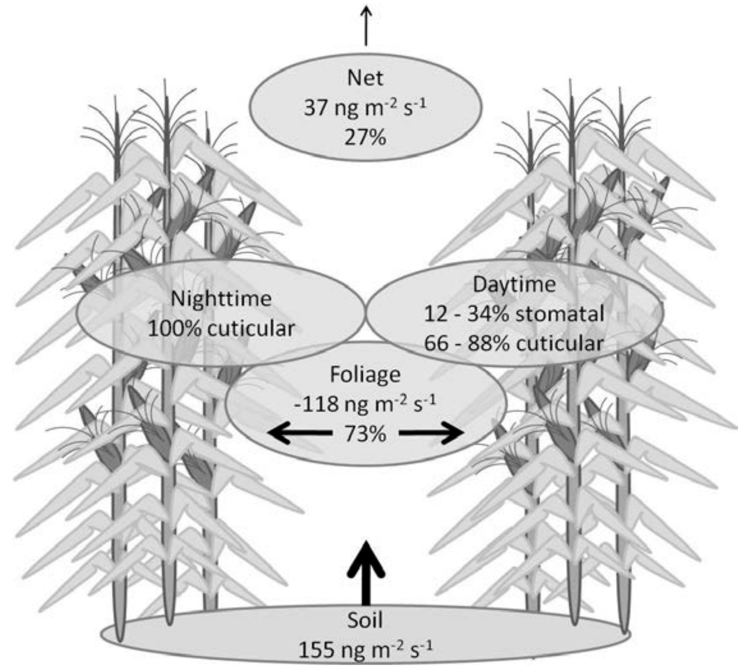

Cuticle
(waxy surface of leaf or needle)
$NH_3$ exchange depends on morphology, acidity and $NH_4^+$ concentrations in surface moisture layers

Stomatal opening
(where $CO_2$ and $H_2O$ are exchanged)

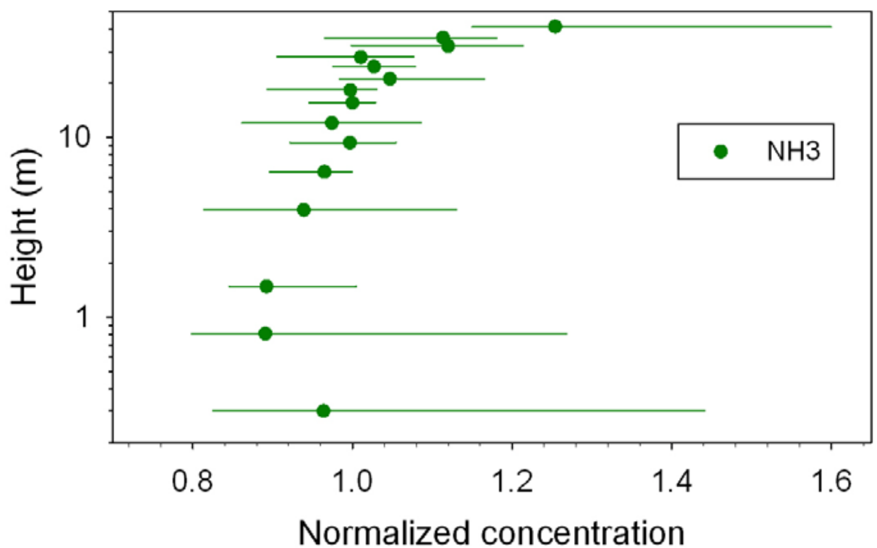
Leaf interior
(apoplast solution)
stomatal $NH_3$ emission potential depends on apoplast concentrations of $NH_4^+$ and $H^+$ and temperature

# Fertilized corn

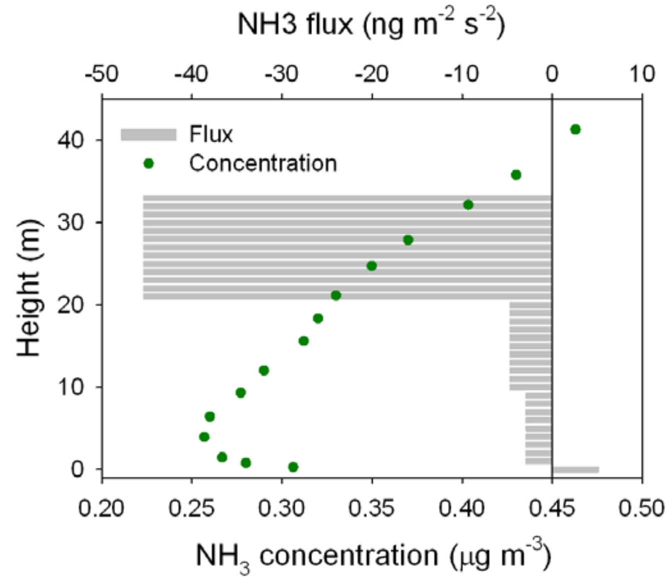



# Mixed hardwood forest



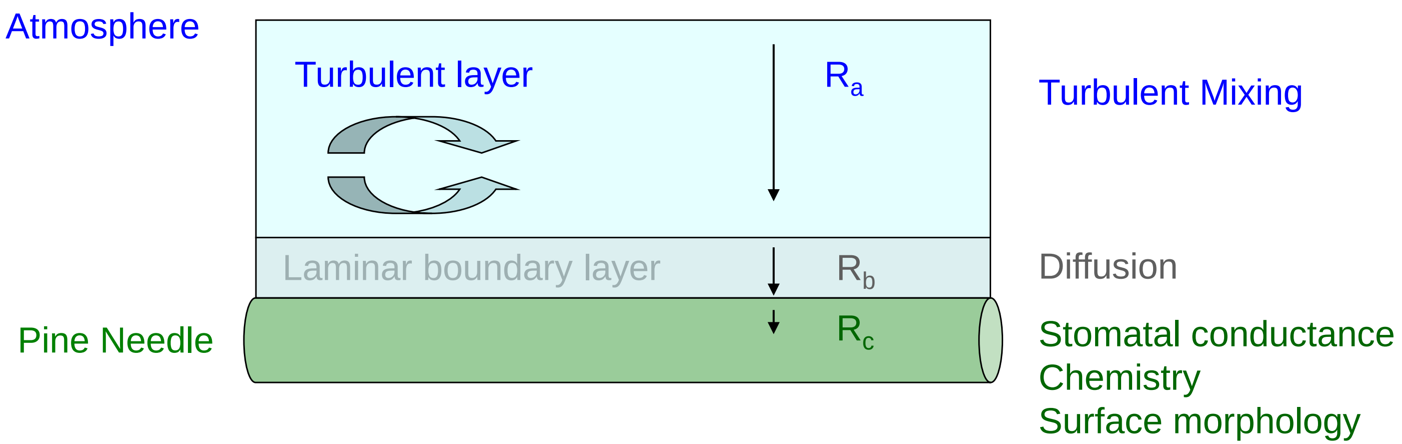

August 11, 2009
900 - 1300

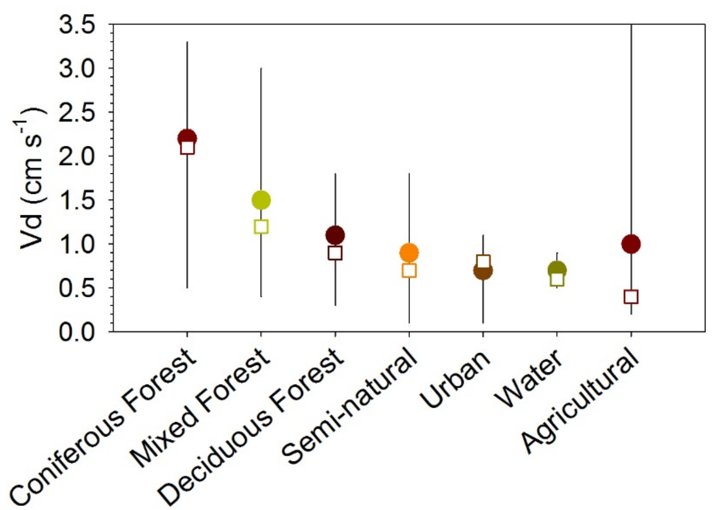


# Deposition Velocity Concept

$$F = -v_d * c \qquad v_d = \frac{1}{R_a + R_b + R_c}$$

- $R_a$ - aerodynamic resistance
- $R_b$ – boundary layer resistance
- $R_c$ – canopy resistance




## Review of deposition velocities across land-use categories

Data from: Schrader, F., Brümmer, C. 2014. Land Use Specific Ammonia Deposition Velocities: a Review of Recent Studies (2004–2013). Water Air Soil Pollut., 225:2114

# Bidirectional Flux Concept

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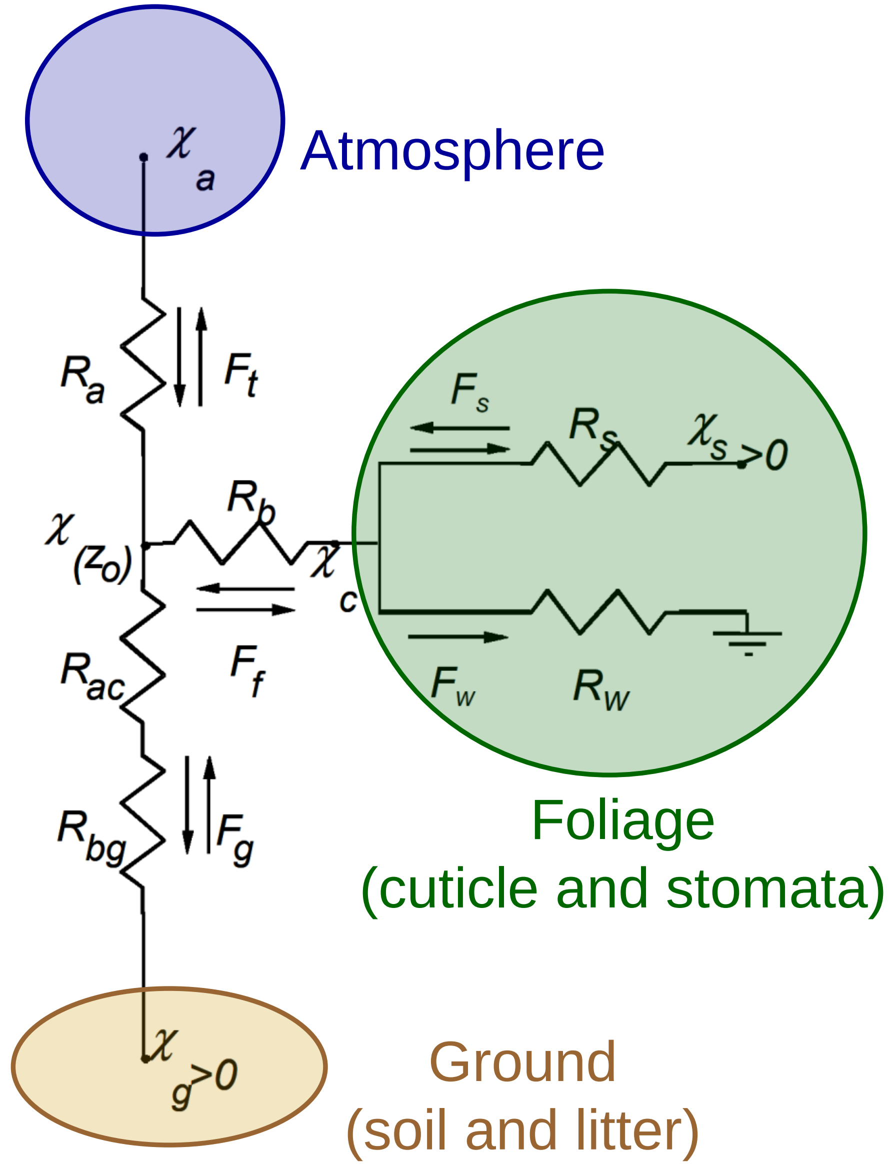
**Resistances**
Aerodynamic ($R_a$)
Boundary layer ($R_b$)
In-canopy ($R_{ac}$, $R_{bg}$)
Stomatal ($R_s$)
Cuticular ($R_w$)

**Compensation points**
Canopy ($\chi_{zo}$)
Stomatal ($\chi_s$)
Ground ($\chi_g$)

**Fluxes**
Net canopy-scale ($F_t$)
Stomatal ($F_s$)
Cuticular ($F_w$)
Foliage ($F_f$)
Ground ($F_g$)



# Methods for Developing Total N Deposition Budgets

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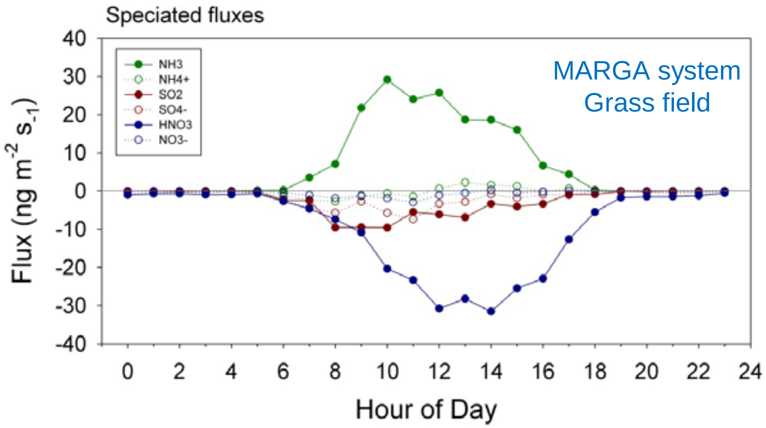
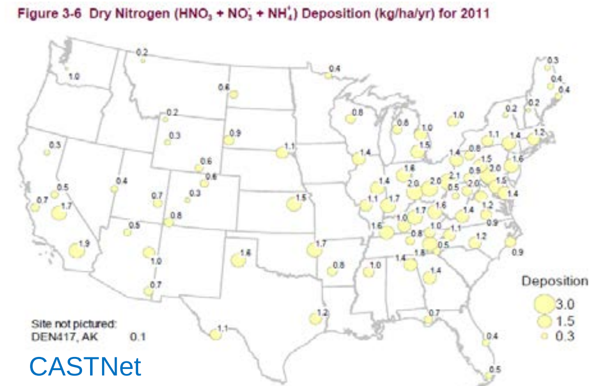
## Flux measurements



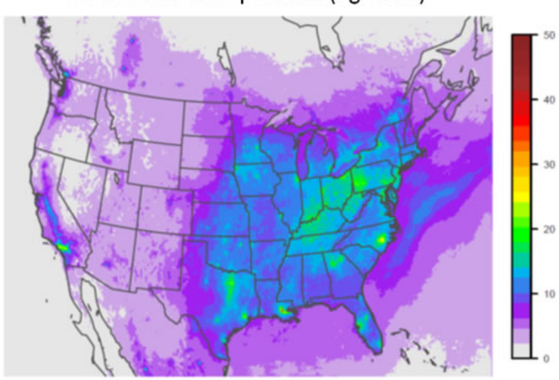

## Field-scale models



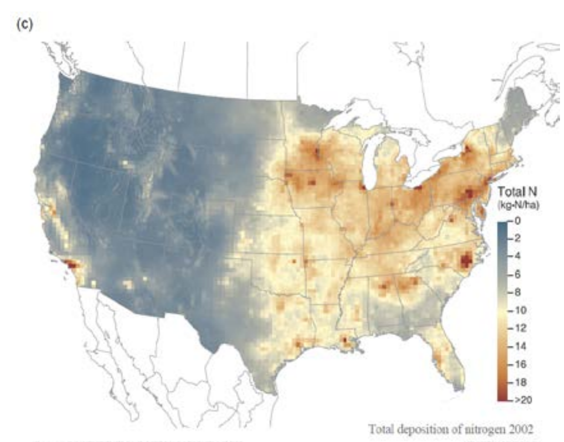

CASTNet
Multi-layer model

## Gridded chemical transport model (CTM)

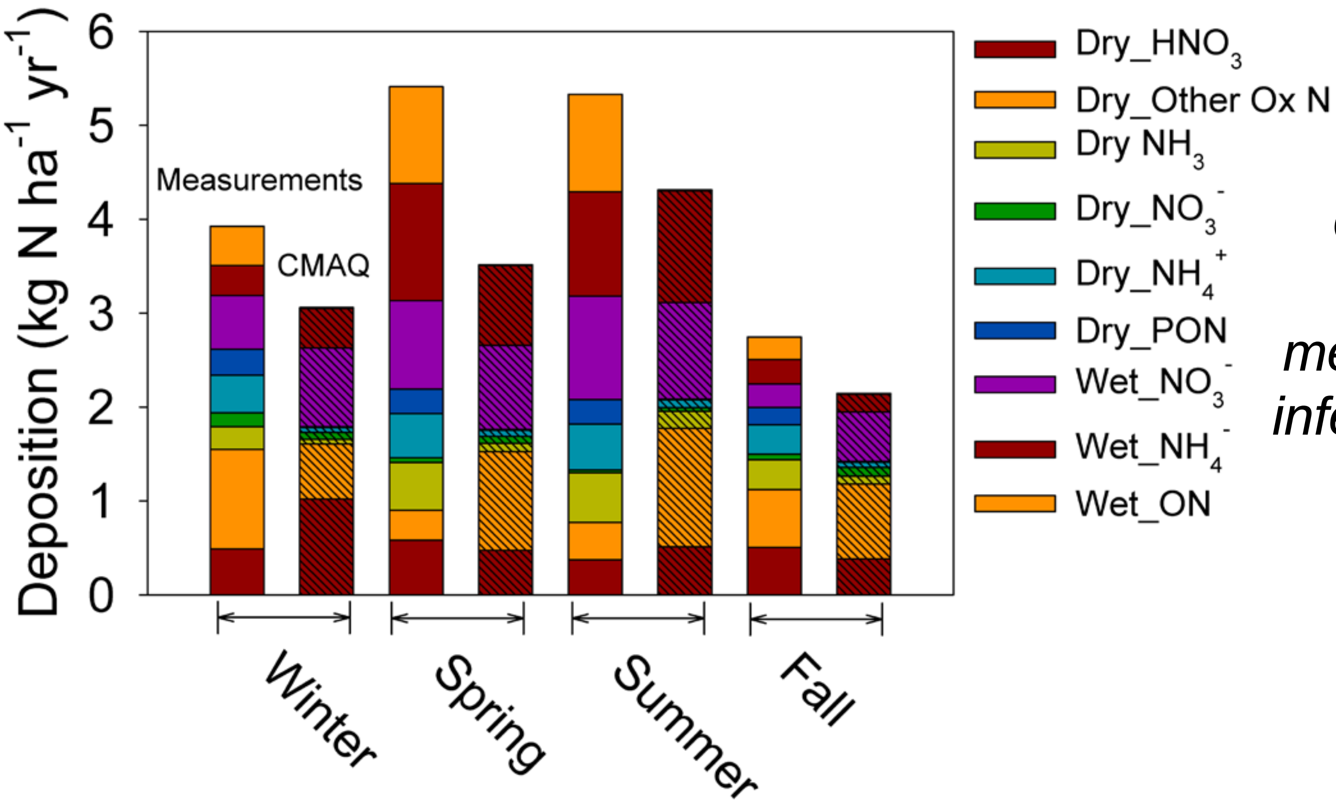
CMAQ with Bi-Directional $NH_3$
2002 Total N Deposition (kg-N/ha)




## Hybrid (Combination of measurements and CTM)



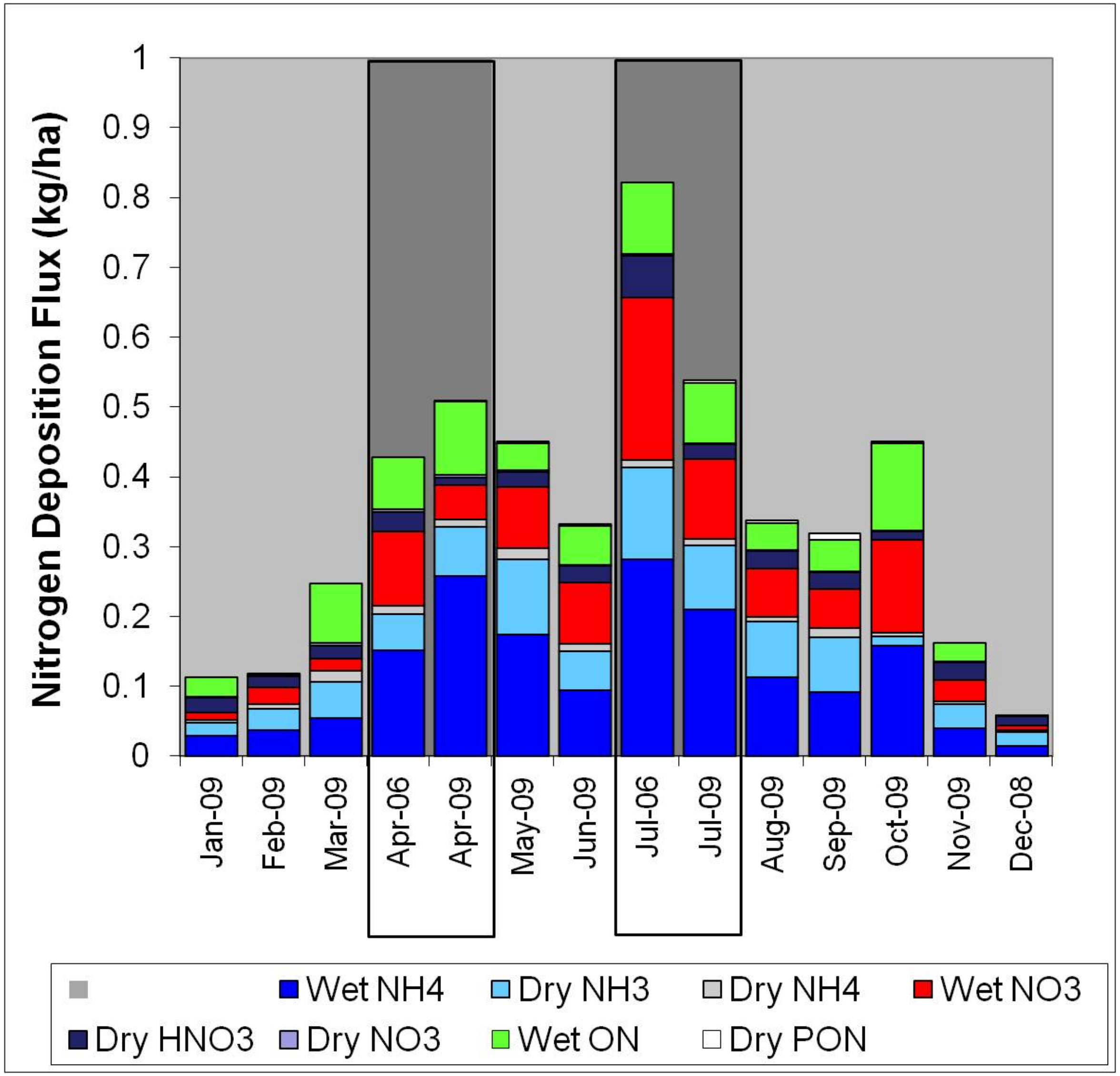
# Field-Scale Models
# Duke Forest




*Combination of direct flux measurements and inferential modeling.*

- In-situ measurements and modeling: Total = 17 kg N ha $^{-1}$ y$^{-1}$
  - $NH_3$ = 9% of total N deposition
- CMAQ unidirectional: Total = 13 kg N ha $^{-1}$ y$^{-1}$
  - $NH_3$ = 3% of total N deposition

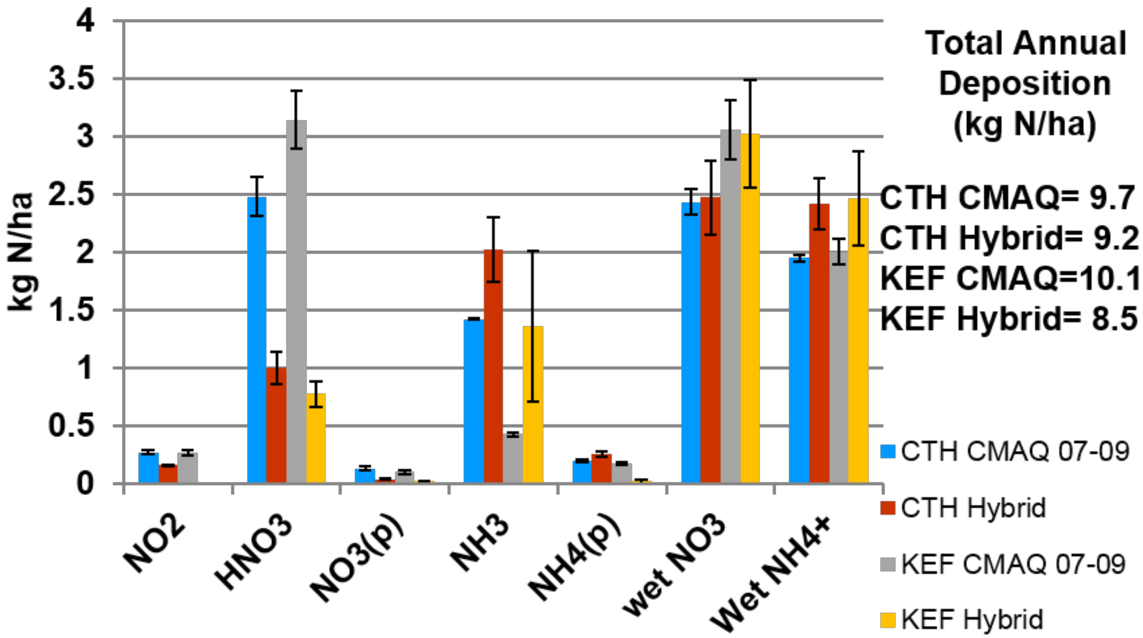
# Field-Scale Models
# Rocky Mountain National Park




- Total N deposition is 3.64 kg N $ha^{-1}$ $yr^{-1}$
- $NH_3$ contributes 18% of total N deposition
- On an annual scale, the deposition budget is dominated by reduced N ($NH_x$ = 53% of total).

KB Benedict, CM Carrico, SM Kreidenweis, B Schichtel, WC Malm 2013. A seasonal nitrogen deposition budget for Rocky Mountain National Park. Ecological Applications 23 (5), 1156-1169

# Field-Scale Models
# Susquehanna River Watershed



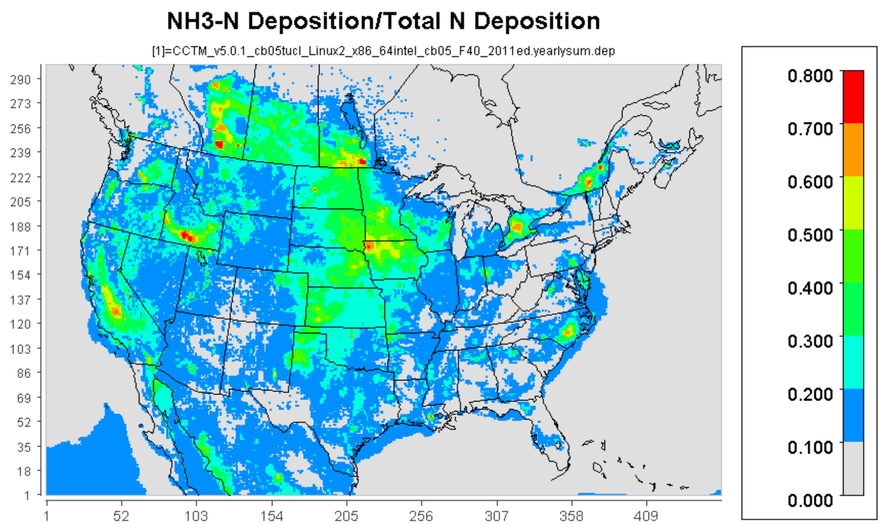

| $NH_3$ as % of total N dep. | |
|---|---|
| CTH CMAQ | 15% |
| CTH Hybrid | 22% |
| KEF CMAQ | 4% |
| KEF Hybrid | 16% |

- CMAQ results indicate that the budget is dominated by oxidized N while the in-situ approach indicates more equivalent contributions from oxidized and reduced nitrogen.

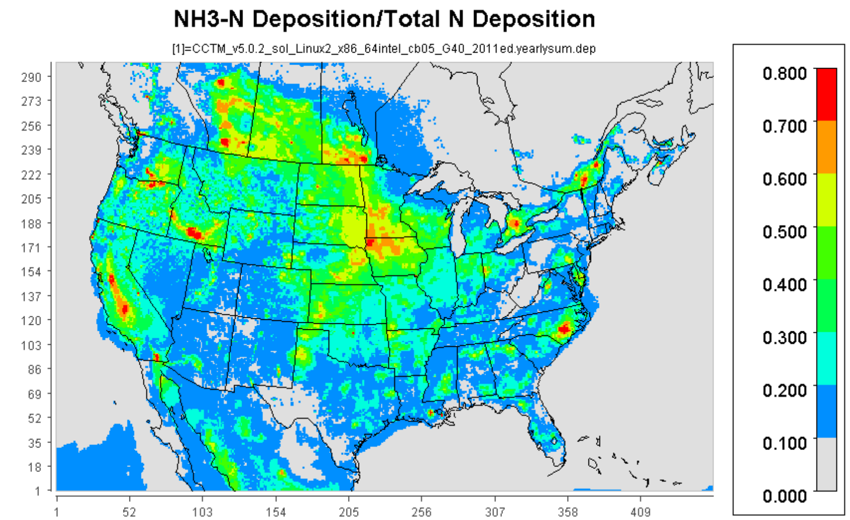

Butler T, Marino R, Schwede D, Howarth R, Sparks J, Sparks K. 2015. Atmospheric ammonia measurements at low concentration sites in the northeastern USA: implications for total nitrogen deposition and comparison with CMAQ estimates. Biogeochemistry (*in press*) DOI 10.1007/s10533-014-0036-5.

# Community-Multiscale Air Quality Model (CMAQ)

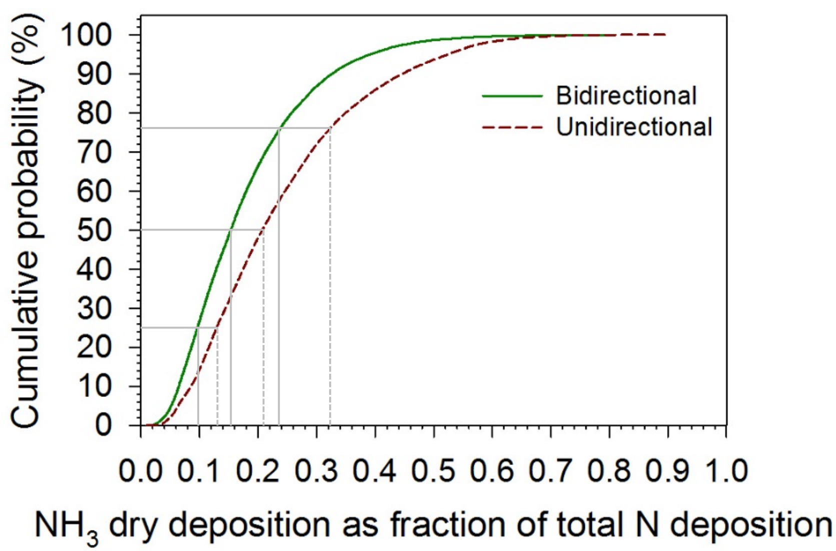
## Bidirectional $NH_3$ flux




## Unidirectional $NH_3$ flux

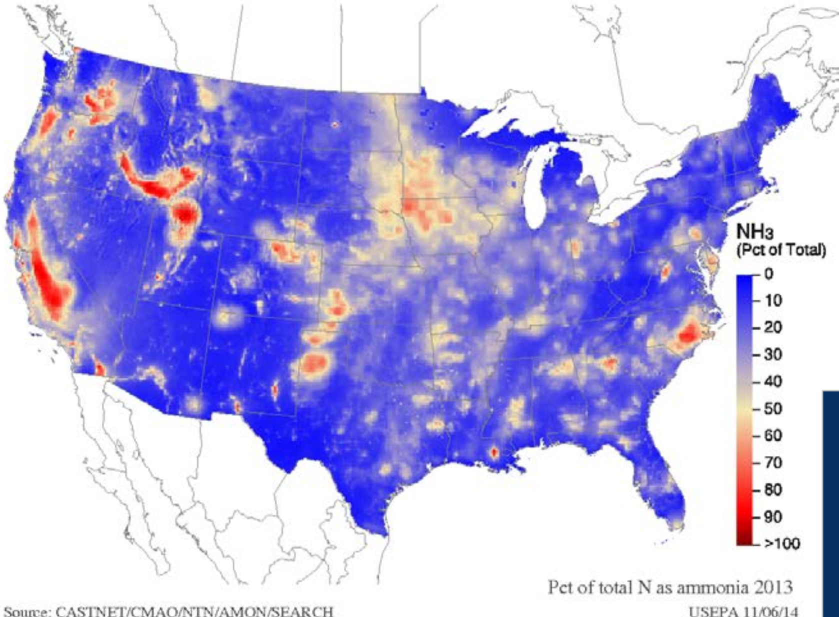



*Cumulative probability plot of fractional contribution of $NH_3$ dry deposition to total N deposition (CONUS)*



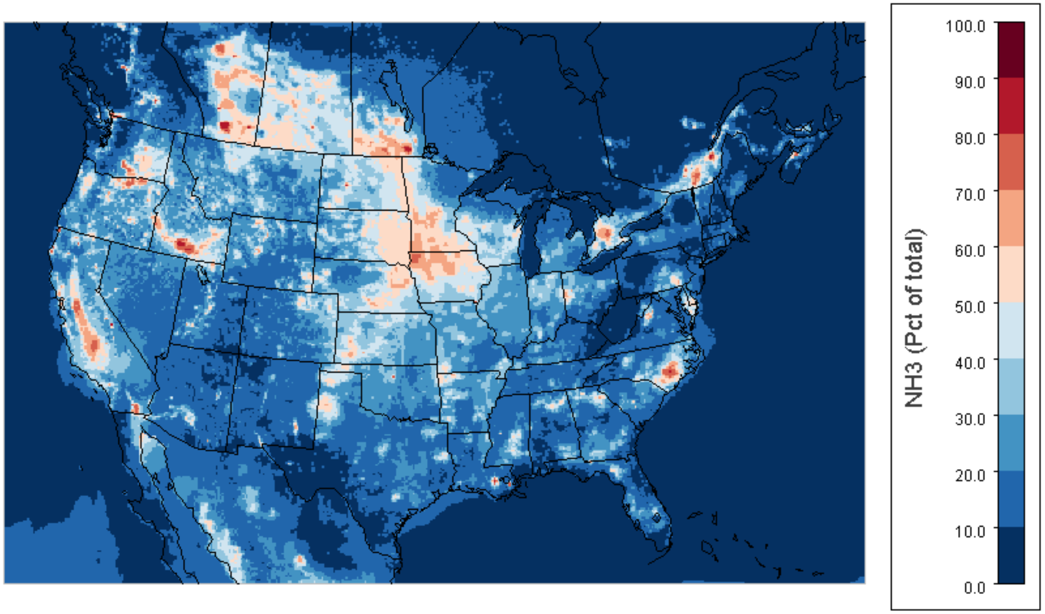
# Hybrid Total Deposition Approach (CMAQ + Monitoring Data)

## Hybrid Total Deposition




*Contribution of $NH_3$ dry deposition to total N deposition*

## CMAQ Unidirectional




Some differences due to incorporation of AMoN $NH_3$ monitoring data in Hybrid approach

*Schwede, D.B. and G.G. Lear, 2014. A novel hybrid approach for estimating total deposition in the United States, Atmospheric Environment, **92**, 207-220.*

# Summary

- Site-specific case studies represent range of deposition conditions:
  - ≈ 17 kg N $ha^{-1}$ $yr^{-1}$ (Duke Forest)
  - ≈10 kg N $ha^{-1}$ $yr^{-1}$ (Upper Susquehanna)
  - ≈ 3.5 kg N $ha^{-1}$ $yr^{-1}$ (Rocky Mountain Nat'l Park)

- The site most highly influenced by urban activities (Duke Forest) exhibits a N deposition budget dominated by oxidized compounds, while the budget at the most remote site (RMNP) is dominated by reduced N species.

- Across these sites, $NH_3$ dry deposition contributes between 3 and 22% of total N deposition.

- Regional-scale modeling indicates that, over 1/2 of the CONUS, $NH_3$ contributes at least 15% of the total N deposition. Over approximately 1/4 of the CONUS, $NH_3$ contributes 25% or more of total N deposition.

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