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 (NH₃) 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 NH₃ to the total pool of reactive nitrogen in the atmosphere and therefore in atmospheric deposition.

• While spatial and temporal patterns of NH₄⁺ wet deposition across the U.S. are relatively well characterized, the contribution of NH₃ dry deposition to total nitrogen deposition is much less certain.

• This presentation explores the state-of-the-science of NH₃ dry deposition and the role of NH₃ 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
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

**Agricultural Ecosystems**

**Natural Ecosystems**
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$_2$O are exchanged)

Leaf interior
(apoplast solution)
stomatal NH$_3$ emission potential depends on apoplast concentrations of NH$_4^+$ and H$^+$ and temperature
**Fertilized corn**

- Canopy height
  - Early morning, $N = 5$
  - Late morning, $N = 11$
  - Afternoon, $N = 8$

**Mixed hardwood forest**

- NH$_3$ flux (ng m$^{-2}$ s$^{-1}$)
  - August 11, 2009
  - 900 - 1300
Deposition Velocity Concept

\[ F = -v_d \ast c \]

\[ v_d = \frac{1}{R_a + R_b + R_c} \]

- \( R_a \) - aerodynamic resistance
- \( R_b \) – boundary layer resistance
- \( R_c \) – canopy resistance

**Atmosphere**

- Turbulent layer
- Laminar boundary layer

**Pine Needle**

- Stomatal conductance
- Chemistry
- Surface morphology

**Turbulent Mixing**

**Diffusion**

**Review of deposition velocities across land-use categories**

Bidirectional Flux Concept

**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

Flux measurements

Field-scale models

Gridded chemical transport model (CTM)

Hybrid (Combination of measurements and CTM)
• 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

Combination of direct flux measurements and inferential modeling.
• 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).

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.

Community-Multiscale Air Quality Model (CMAQ)

Bidirectional NH₃ flux

Cumulative probability plot of fractional contribution of NH₃ dry deposition to total N deposition (CONUS)

Unidirectional NH₃ flux
Hybrid Total Deposition Approach (CMAQ + Monitoring Data)


Some differences due to incorporation of AMoN NH$_3$ monitoring data in Hybrid approach.
Summary

- Site-specific case studies represent range of deposition conditions:
  - $\approx 17$ kg N ha$^{-1}$ yr$^{-1}$ (Duke Forest)
  - $\approx 10$ kg N ha$^{-1}$ yr$^{-1}$ (Upper Susquehanna)
  - $\approx 3.5$ 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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