# Investigation of ammonia air-surface exchange processes in a deciduous montane forest in the southeastern U.S.

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#### *Motivation for studying NH*<sup>3</sup> *air-surface exchange*

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- Nitrogen (N) deposition shifting from a predominance of oxidized to reduced (NH<sub>x</sub>) forms
- NH<sub>3</sub> important to N deposition budget in many areas
- NH<sub>3</sub> dry deposition much more uncertain than wet NH<sub>4</sub><sup>+</sup> deposition
- National deposition assessments rely on complex atmospheric models
- NH<sub>3</sub> dry deposition model algorithms are very uncertain

Source: CASTNET/CMAQ/NTN/AMON/SEARCH

# Contribution of NH<sub>3</sub> dry deposition to total N deposition

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.

#### Why Coweeta?



- NH<sub>3</sub> concentrations at Cowéeta Hydrologic Laboratory are low
- Low concentrations *should* provide an opportunity to observe the "bi-directional" nature of NH<sub>3</sub> air-surface exchange

#### **Objectives and Methodology**

#### Southern Appalachian Nitrogen Deposition Study (SANDS)

*Combination of measurements and modeling to quantify air-surface fluxes and characterize processes* 



- Continuous direct measurement of net canopy-scale flux using online ion-chromatography
  - total flux to/from forest
- Measurement of air concentrations and flow at multiple heights within canopy to estimate vertical source/sink profiles
  - canopy versus forest floor
- Measurement of green leaf, soil, and litter chemistry
  - Characterization of NH<sub>3</sub> emission potentials

#### **Objectives and Methodology**

- A primary objective of SANDS is to improve parameterizations of soil and vegetation emission potentials used in bidirectional NH<sub>3</sub> air-surface exchange models.
- This presentation explores aspects of soil and vegetation chemical measurements during year 1 of SANDS (2015) and implications for compensation point parameterizations.
- The potential impact of the updated parameterizations on seasonal and annual modeled NH<sub>3</sub> fluxes is assessed by comparing 1 year simulations of different model configurations:
  - Base bidirectional flux model using Massad et al (2010) parameterization
  - Modified stomatal emission potential
  - Modified soil/litter emission potential

#### Conceptual model of NH<sub>3</sub> air-surface exchange in a forest



#### Base NH<sub>3</sub> model configuration

- Two-layer (vegetation soil) compensation point framework of Nemitz et al (2001). Fundamentally similar to CMAQ bi-directional model.
- Compensation points
  - Vegetation emission potential ( $\Gamma_s$ ) parameterized according to Massad et al. (2010) as a function of total nitrogen deposition
  - Soil assumed to have constant emission potential of  $\Gamma_q = 20$
- Resistances (above- and in-canopy) parameterized according to Massad et al. (2010), Wesely (1989)
- Canopy zo, zd, LAI follow MLM specifications (Meyers et al., 2998)
- Meteorology wind speed, friction velocity measured by sonic anemometer (above canopy and at 2 m above forest floor).
- NH<sub>3</sub> concentrations 2015 AMoN
- 1 year simulation of hourly net and component (leaf stomata, leaf cuticle, and ground) - 2015

#### NH<sub>3</sub> concentrations



- 2015 spatial variability study examined NH<sub>3</sub> concentrations along an elevation gradient from 683 m (NC25) to 1143 m (CS77) within the Coweeta basin.
- Overall variability low. No clear trend with elevation. NC25 and EFT similar.
- 2015 concentrations at NC25 lower than historical values



#### Base NH<sub>3</sub> model results



- Blank correcting the NH $_3$  concentration (0.1 µg m<sup>-3</sup>) reduces the net annual flux to -0.38 kg N ha<sup>-1</sup>
- At lower atmospheric NH<sub>3</sub> concentration, net emission is observed in the summer

- Net annual flux = -0.38 kg N ha<sup>-1</sup> (deposition)
- Largest deposition rates to leaf cuticle
- Net emission from leaf stomata during all seasons



#### Base model – NH3 blank corrected

#### In-canopy air chemistry profiles (day)



- Highest air concentrations occur in upper canopy
- Concentrations decrease from the canopy to the atmosphere
- Concentrations decrease from the upper canopy through the understory
- Concentrations increase again just above the ground

## Measured emission potential ( $\Gamma_{\rm stomata}$ ) of vegetation

 $\chi_{ston}$ 

Stomatal compensation point

$$\frac{161500}{a^{ta}} \exp\left(-\frac{10380}{T}\right) \underbrace{\left[NH_{4}^{+}\right]}_{\left[H^{+}\right]}$$

# Emission potential $(\Gamma_{stomata})$

$$\Gamma_s = 19.3e^{0.0506[NH_4^+]_{bulk}}$$
 Massad et al., 2010

#### Green leaves

Species	µg NH <sub>4</sub> +/g tissue	$\Gamma_{stomata}$	χ <sub>stomata</sub> @25degC
Mt. Laurel	2.5	22	0.15
Rhododendron	4.9	25	0.17
White Pine	6.6	27	0.19
Maple	12.7	37	0.25
Beech	16.2	44	0.30
White Oak	16.4	44	0.30

Base model parameterization predicts  $\Gamma_{stomata}$  10X larger ( $\approx$  250)

#### Emission potential of forest floor



Profiles indicate source of NH<sub>3</sub> at forest floor. Is this a litter or soil process?

Measurements of soil extractable  $NH_4^+$  and pH indicate an emission potential  $(\Gamma_{soil}) \sim 10$  $\chi_{soil}$  @ 25 °C ~ 0.1 µg m<sup>-3</sup>

Measurements of litter soluble  $NH_4^+$  indicate an emission potential ( $\Gamma_{litter}$ ) ~ 200  $\chi_{litter}$  @ 25 °C ~ 1.4 µg m<sup>-3</sup>

Most likely the litter.

Base model does not consider litter, only soil.

### Modified model configuration

• Base model with blank correction was modified to include lower measured stomatal emission potential ( $\Gamma_s$ ) and by replacing soil emission potential with litter emission potential ( $\Gamma_l$ ).



- Adding  $\Gamma_l$  results in a net emission from the forest floor.
- Reduces net annual flux to -0.28 kg N ha<sup>-1</sup>

- Net annual flux = -0.45 kg N ha<sup>-1</sup> (deposition) compared to
- Lowering the leaf emission potential reduces stomatal emissions, thereby increasing net deposition rates.



#### Conclusions

• Measured leaf  $NH_3$  emission potentials show large interspecies variability and overall average values are a factor of 5 – 10 lower than the currently used parameterization.

Measured emission potential of the leaf litter is approximately a factor of 20 larger than the emission potential of the underlying mineral soil.

 Modifying the currently used bidirectional NH<sub>3</sub> exchange model to incorporate a lower leaf emission potential and adding a litter emission potential reproduces patterns of in-canopy fluxes inferred from air concentrations.

• Results suggest that refinement of the model based on measured biogeochemical  $NH_4^+$  pools will result in significantly lower net deposition rates to the ecosystem than currently predicted.

## Next steps for SANDS NH<sub>3</sub> analysis

• Examine temporal variability in emission potentials derived from seasonal soil/litter/leaf sampling

• Combine in-canopy air concentration and turbulence data to estimate source/sink profiles within the canopy

• Calculate fluxes from above-canopy continuous gradient system and compare with source/sink estimates

• Compare net canopy-scale fluxes from current air-surface exchange model with measured fluxes and source/sink estimates

• Update recommendations for modified model parameterizations

 $\bullet$  Evaluate importance of seasonal/annual  $\rm NH_3$  fluxes within context of N deposition budget

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