Chemical surface-atmosphere exchanges: experimental approach and modeling

Nebila Lichiheb

NOAA Air Resources Laboratory

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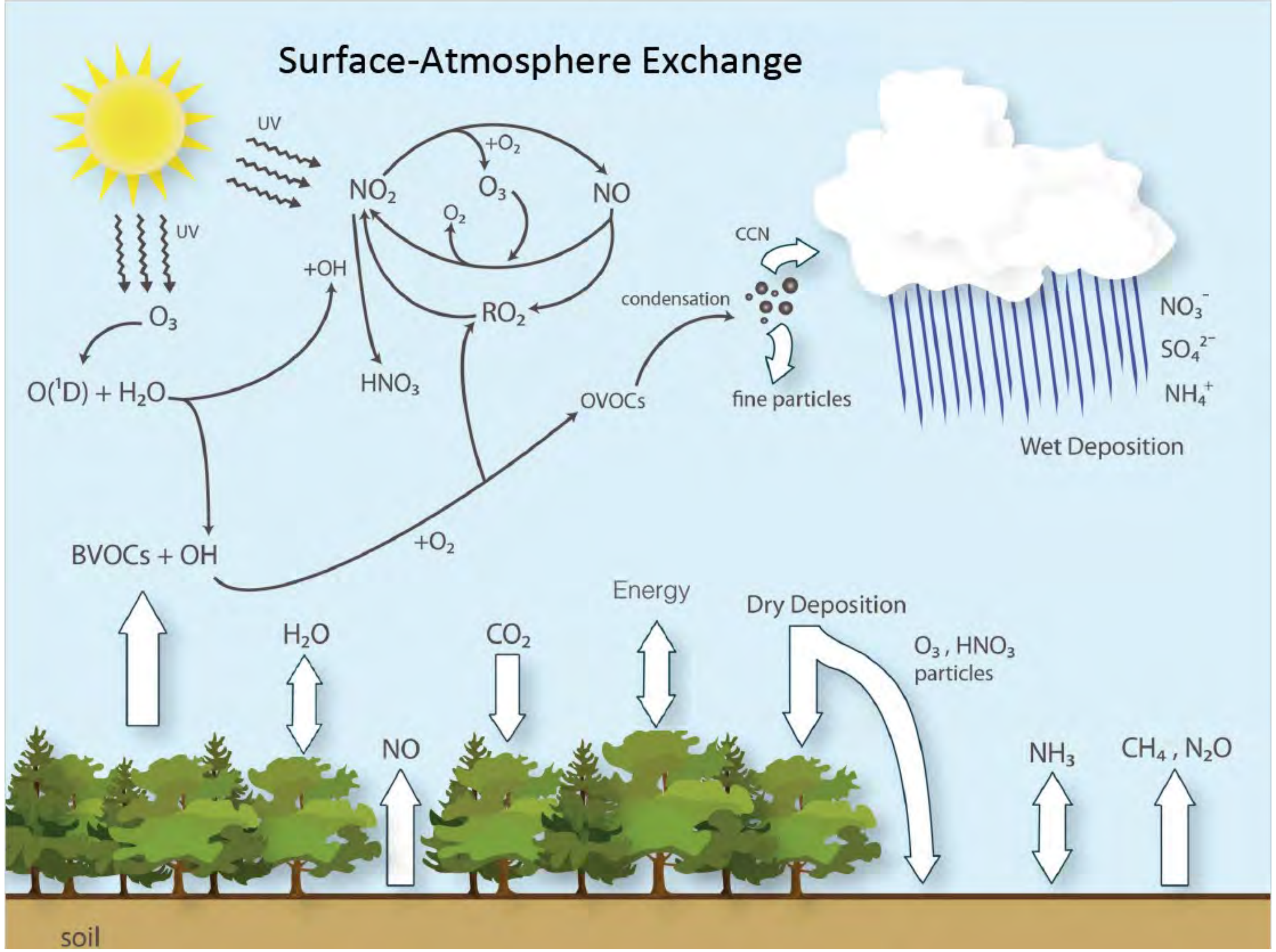
Background: Biosphere – Atmosphere Interactions

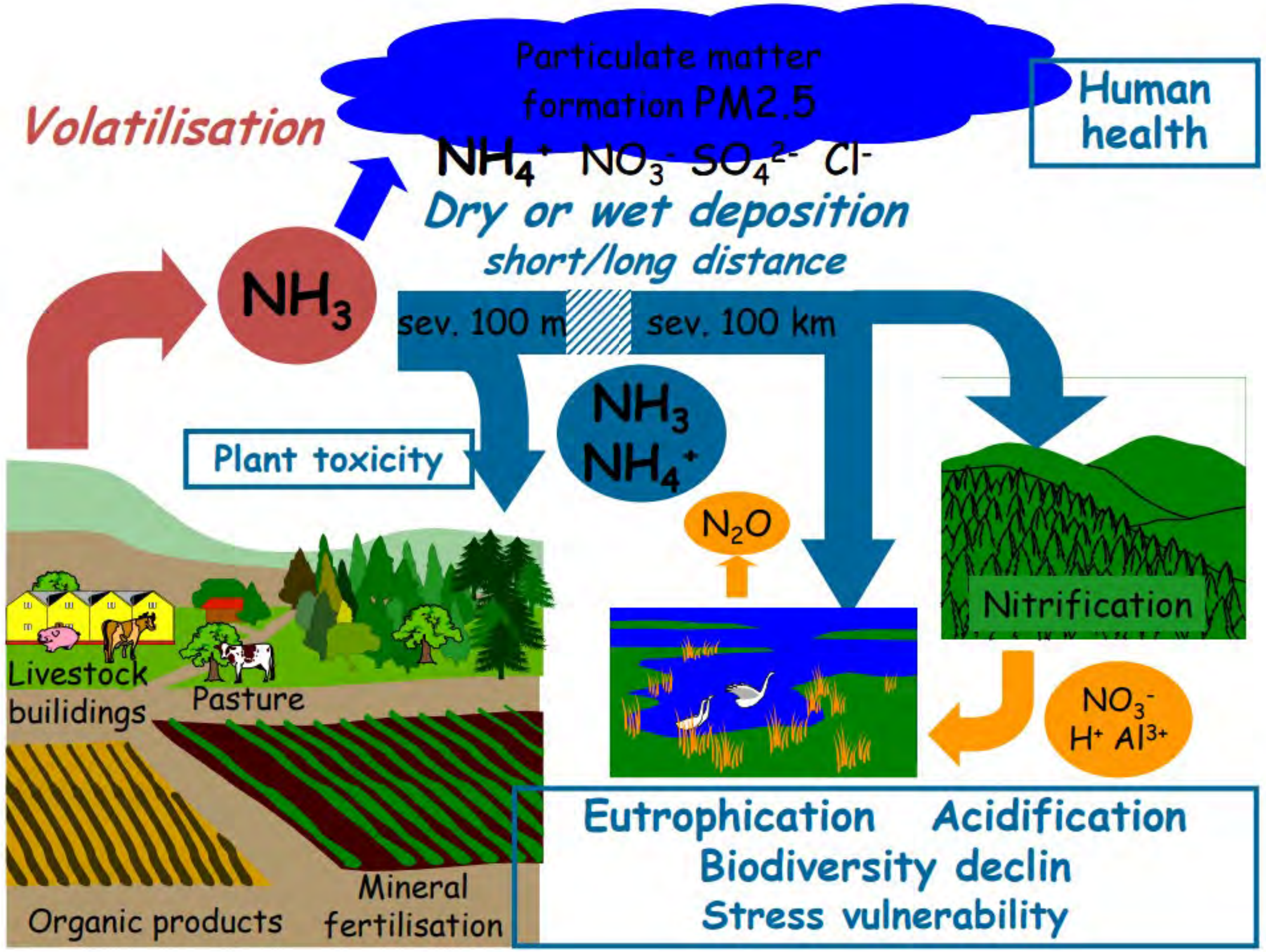


- Chemicals can be emitted from **Natural** (VOCs, CO_2) or **Anthropogenic** (SO…) sources.
- Other chemicals are formed in the atmosphere and are taken up by the vegetation (O_3).
- The exchange of the chemicals between the atmosphere and Earth's surface can be **Unidirectional** (CH_4, NO) or **Bidirectional** (NH_3).

- Understand how specific emissions lead to pollutant formation that are then deposited far downwind.

- Investigating the biosphere-atmosphere exchanges of chemicals is fundamental to understand atmospheric chemistry, hydrological and biogeochemical cycles.

Background: Why reactive nitrogen (specifically NH_3)?



The environmental impact of NH_3

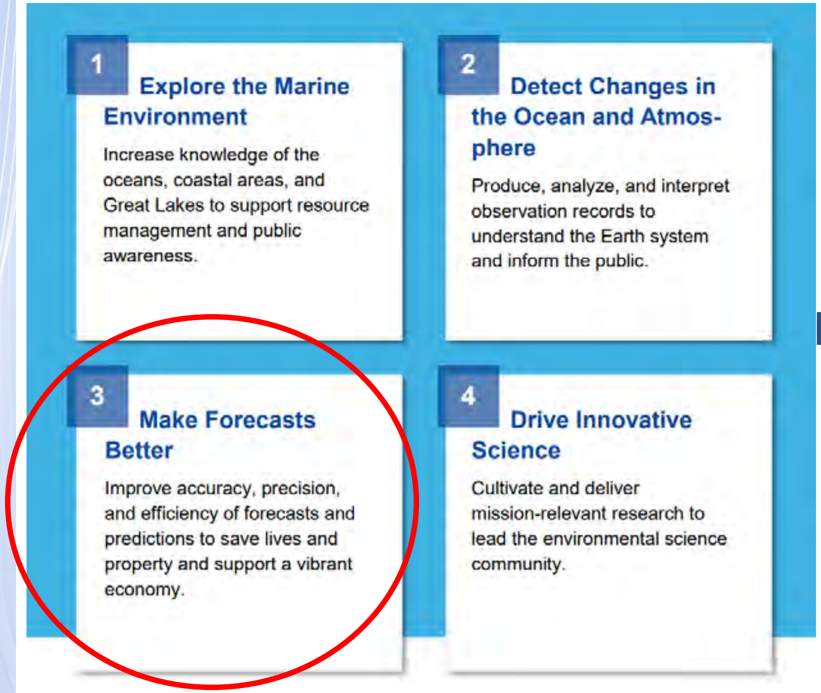
- The accumulation of reactive nitrogen (Nr) is a global environmental issue impacting water quality, human and ecosystem health and greenhouse gas emissions: The Nitrogen Cascade (Galloway *et al.*, 2003).
- Ammonia (NH_3) is a key component of the biogeochemical cycle: It is the most challenging reactive nitrogen compound due to its bidirectionality.
- The United States is one of the world's leading producers and consumers of NH_3:
  - The agricultural sector contributes approximately 85% of U.S. NH_3 emissions (US EPA, 2021);
  - Fires account for 8% of NH_3 emissions in the U.S (US EPA, 2021)… .

- The monitoring of atmospheric NH_3 remains limited.

- Mechanisms for the bidirectional exchange of NH_3 are poorly understood: Large uncertainties in model forecasts.

Where does this research fit within NOAA's mission ?

OAR strategy goals



Goal 3: Make Forecasts Better

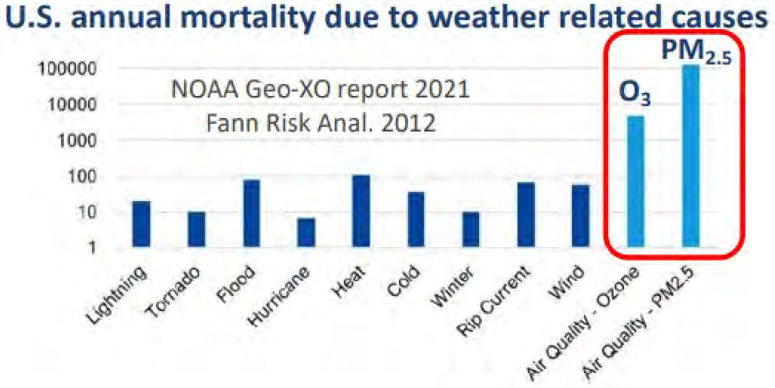
3.1. Develop interdisciplinary Earth system models.

3.2. Design tools and processes to forecast high-impact weather, water, climate, ocean, and ecosystem events.

3.3. Transition science that meets users' current and future needs.

(Strategic Plan 2021-2026)

Air Quality Research



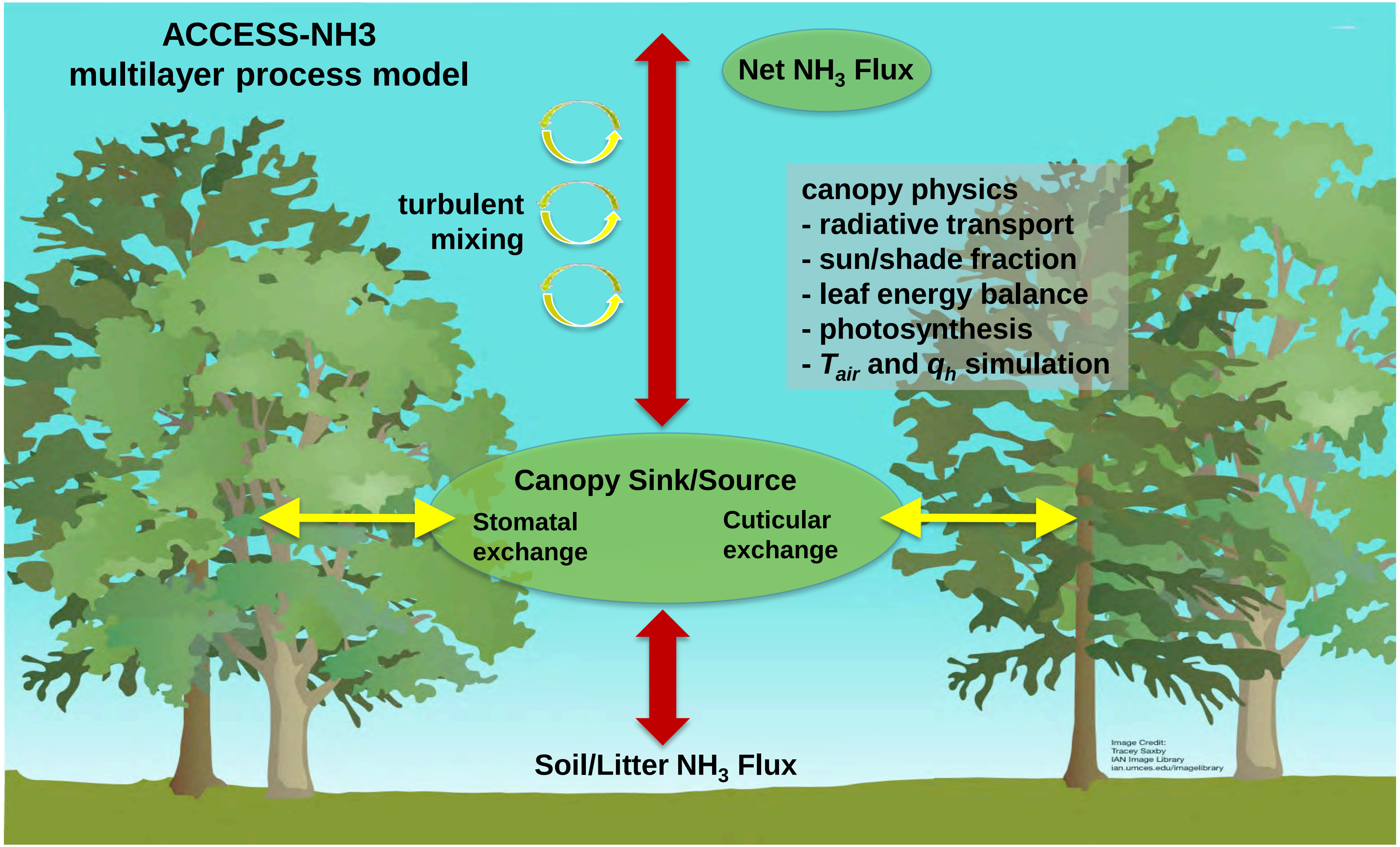
Nr (specifically NH_3) participates in the formation and growth of $PM_{2.5}$.

Air Quality is a costly and deadly issue affecting millions of people in the U.S. and billions globally.

- **The goal of this research is to refine the estimation of air pollution and assess the risks to human health and the environment: Integrated measurement and modelling approaches.**
- **Improve surface-atmosphere exchange processes in Air Quality (AQ) forecasts and in the Unified Forecast System (UFS) models.**

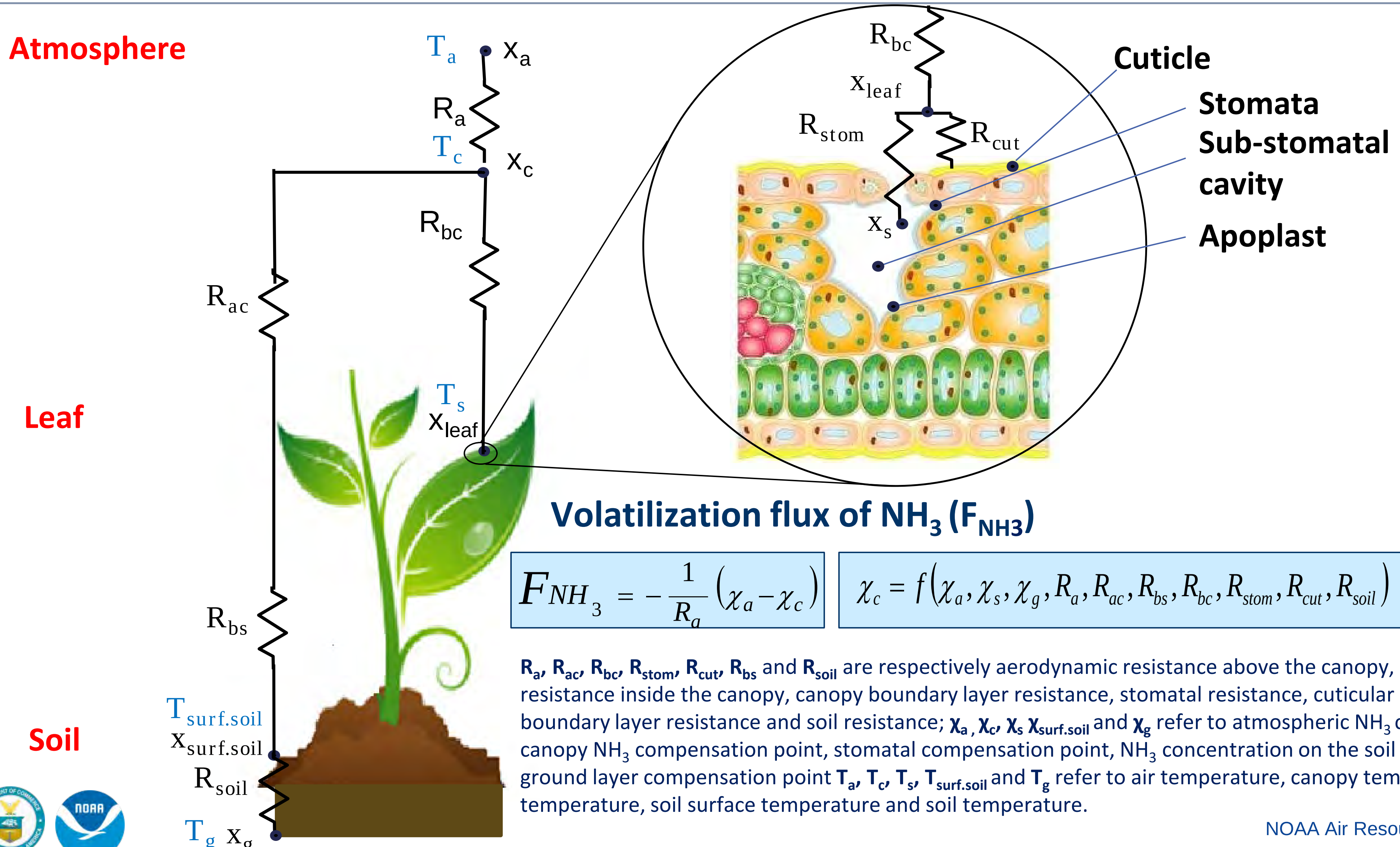
ACCESS-NH_3

Atmospheric Chemistry and Canopy Exchange Simulation System (ACCESS) (Saylor, 2013)



SURFATM-NH_3 (Personne et al., 2009)

Collaboration with Dr. Erwan Personne: UMR ECOSYS INRA-AgroParisTech (Paris, France)



Volatilization flux of NH_3 (F_{NH3})

$$F_{NH_3} = -\frac{1}{R_a}(\chi_a - \chi_c)$$

$$\chi_c = f(\chi_a, \chi_s, \chi_g, R_a, R_{ac}, R_{bs}, R_{bc}, R_{stom}, R_{cut}, R_{soil})$$

R_a, R_{ac}, R_{bc}, R_{stom}, R_{cut}, R_{bs} and **R_{soil}** are respectively aerodynamic resistance above the canopy, aerodynamic resistance inside the canopy, canopy boundary layer resistance, stomatal resistance, cuticular resistance, soil boundary layer resistance and soil resistance; **χ_a, χ_c, χ_s $\chi_{surf.soil}$** and **χ_g** refer to atmospheric NH_3 concentration, canopy NH_3 compensation point, stomatal compensation point, NH_3 concentration on the soil surface and the ground layer compensation point **T_a, T_c, T_s, $T_{surf.soil}$** and **T_g** refer to air temperature, canopy temperature, leaf temperature, soil surface temperature and soil temperature.

NH_3 exchanges over an agricultural ecosystem

Collaboration with Dr. Sotiria Koloutsou-Vakakis & Dr. Mark Rood: University of Illinois at Urbana-Champaign (Urbana, IL)

Objective: Quantify & investigate above canopy NH_3 concentrations and fluxes from fertilized corn field in the Midwestern USA.

Location: Energy Farm at the University of Illinois at Urbana-Champaign, IL.

Study period: From 6 May to 31 July, 2014.

Model simulations: 2016 – 2017.

Funding source: NSF.

REA sampling system

Relaxed Eddy Accumulation (REA)

Concept: quantify total number molecules in updraft & downdraft at a fixed point to determine flux for a scalar.

$$\overline{F_{REA}} = \beta\sigma_w\left(\overline{C^{\uparrow}} - \overline{C^{\downarrow}}\right)$$

$\overline{F_{REA}}$ is the vertical turbulent flux, β is the REA coefficient, σ_w is the standard deviation of the vertical wind velocity, C is concentration, ↑ and ↓ denote up- and down-draft measurements..

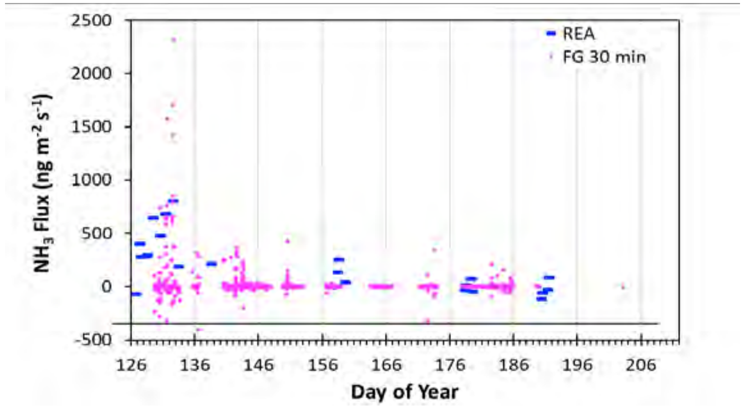
Flux-gradient (FG)

Concept: determines emission and deposition fluxes from vertical gradient of air concentrations.

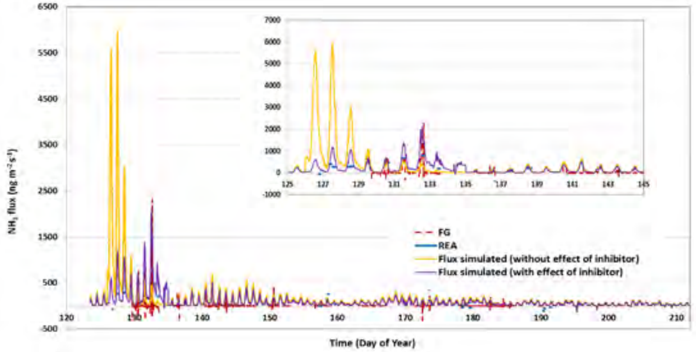
$$F_{FG} = -K_c\left(\frac{\Delta C}{\Delta z}\right)$$

F_{FG} is the flux from FG, K_c is the eddy diffusivity for the pollutant, ΔC is the vertical concentration gradient, and Δz is the vertical distance.

FG sampling system



NH_3 fluxes measured using REA and FG techniques



Modeled NH_3 flux simulated by SURFATM-NH_3

- **NH_3 flux measurements using several micrometeorological techniques over a corn canopy.**
- **New parameterization of the effect of urease inhibitor on NH_3 emissions from urea-based fertilizers.**

Atmospheric NH_3 measurements over a coastal ecosystem

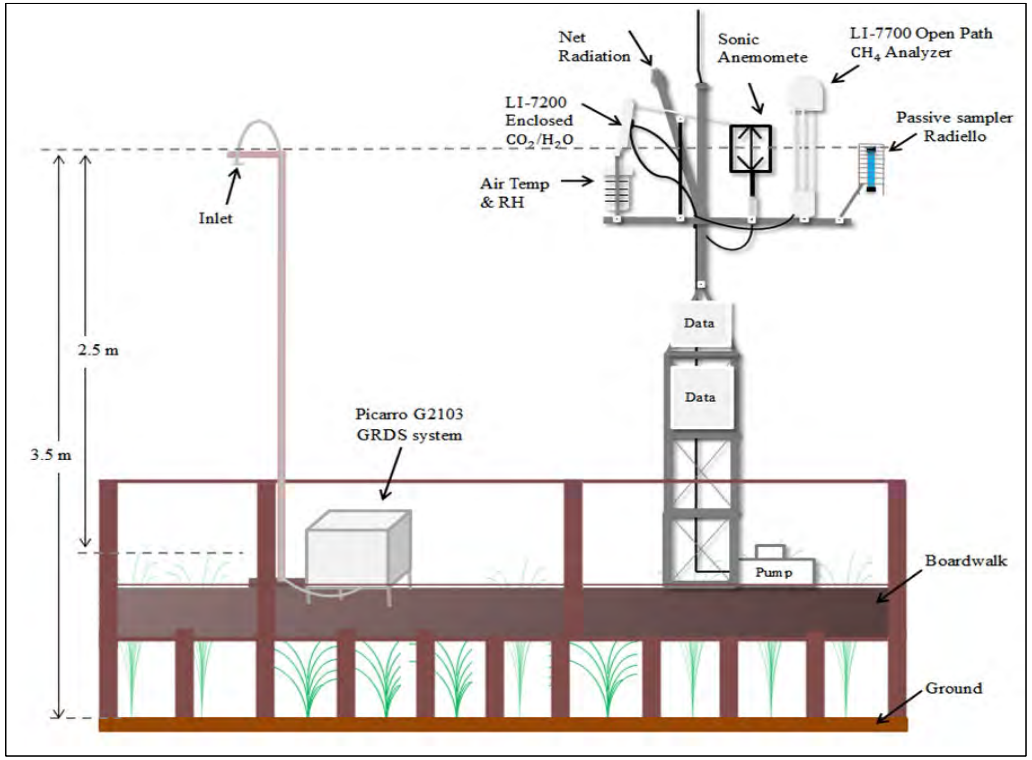
Collaboration with Dr. St. Laurent: Delaware National Estuarine Research Reserve (Dover, DE) & Dr. Vargas : University of Delaware (Newark. DE)

Objective: Advance our process-level understanding of NH_3 air-surface exchange over a coastal salt marsh along the Mid-Atlantic U.S.

Location: The St Jones Reserve, Dover, DE.

Study period: From 21 June to 20 July 2018.

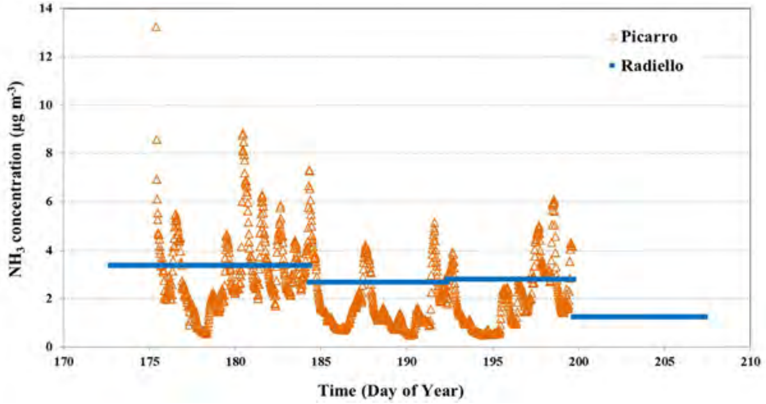
Funding source: NOAA.



Schematic of the experimental set-up

CRDS system

Radiello passive sampler



Measured NH_3 concentrations

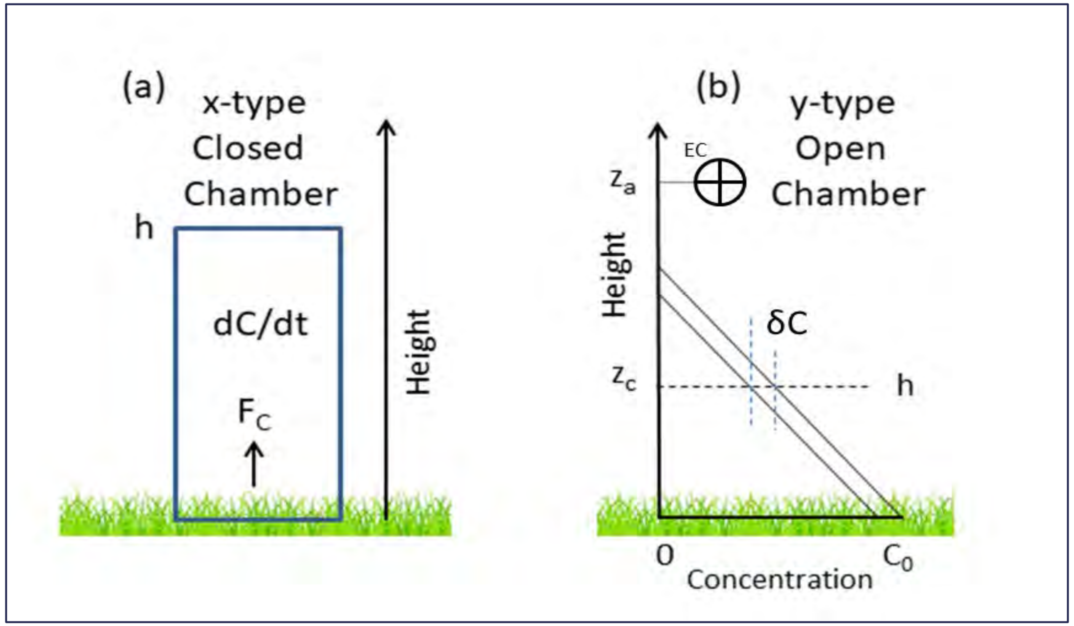
- **One of the few atmospheric measurements of NH_3 over a tidal salt marsh in the Mid-Atlantic U.S.**
- **Salt marshes could be a sink of NH_3 via atmospheric deposition or a source of NH_3 in anaerobic and aerobic conditions.**

The virtual chamber statistical concept

Collaboration with Mr. Bruce Hicks: MetCorps (Norris, TN) & Dr. Neal Eash: University of Tennessee (Knoxville, TN)

Objectives

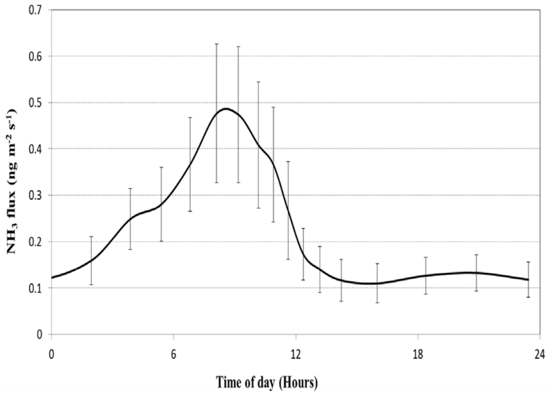
- Propose a new statistical approach to provide a solution to estimate surface fluxes in continuing strongly stable conditions, such as are often encountered over land at night and over wetlands in daytime.
- Estimate the average diurnal cycle of NH_3 fluxes at the St Jones reserve site.



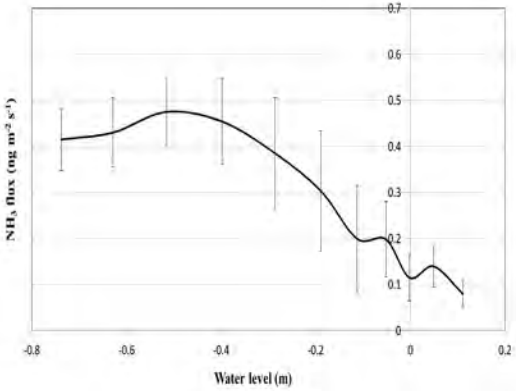
Schematic illustrations of the virtual chamber method

Assuming a solid lid across the top of the tidal marsh, extending from edge to edge at height (**h**). If the flux from the surface of NH_3 (**F_{NH3}**) was constant, the concentrations of NH_3 (**C_{NH3}**) within the confined layer would increase as determined by the wind speed (**u**) and the distance from the upwind edge (**x**).

$$F_{NH_3} = C_{NH_3} h(u/x)$$



Average diurnal cycle of NH_3 fluxes



Average diurnal cycle of NH_3 fluxes as a function of tidal depth.

Tidal depth has a significant effect on NH_3 emissions: the highest NH_3 fluxes were observed at low tide when more soil/island was exposed.

Bi-directional exchanges of NH_3 over a deciduous forest canopy

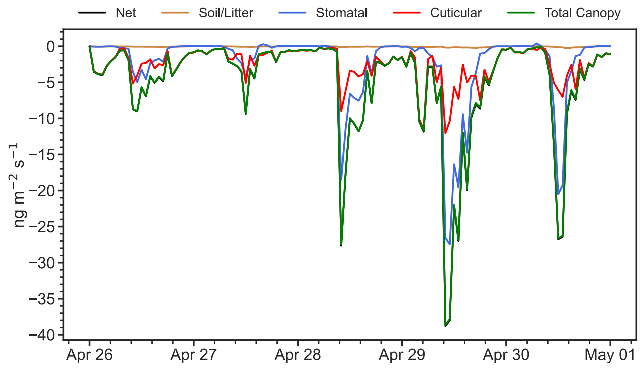
Collaboration with Dr. John Walker: U.S. EPA (Durham, NC)

Objectives: Advance Southern Appalachian Nitrogen Deposition Study (SANDS): Combination of measurements and modeling to quantify nitrogen air-surface fluxes and characterize processes.

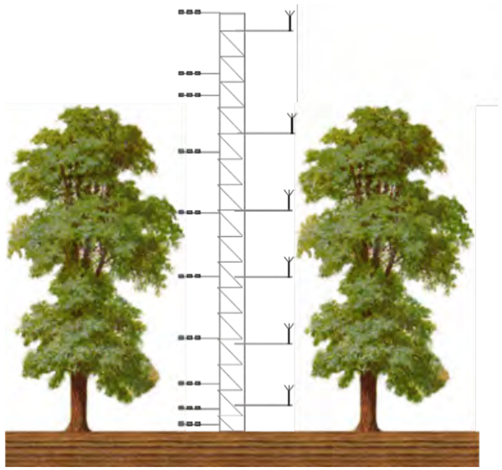
Location: U.S. Forest Service, Coweeta Hydrologic Laboratory, southwestern NC.

Study period: From May 21 - June 9, 2015; August 6 – 25, 2015; September 9 – 26, 2015; April 19 – May 11, 2016; and July 13 – August 3, 2016.

Funding source: U.S. EPA.



*NH_3 fluxes simulated with **ACCESS-NH_3** model*



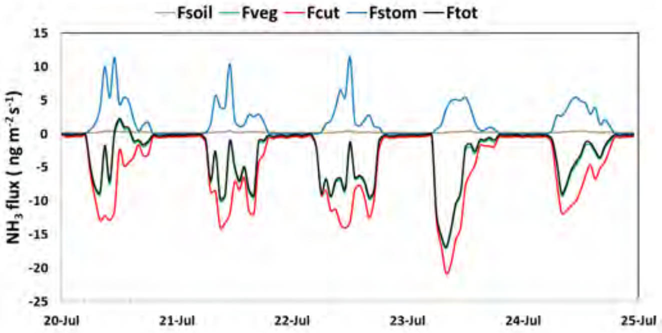
Eddy Flux Tower

Mixed hardwood forest with evergreen understory.

Air : NH_3 concentration (denuder and MARGA data), wind speed, friction velocity, sensible and latent heat flux, chemical fluxes, solar radiation, rainfall, air temperature.

Canopy: height, LAI, NH_3 emission potentials, green leaf and litter chemistry.

Soil: temperature, moisture, pH, heat flux, soil chemistry, NH_3 emission potentials.



*NH_3 fluxes simulated with **SURFATM-NH_3** model*

- **ACCESS-NH_3 and SURFATM-NH_3 can reasonably reproduce NH_3 fluxes over a forest canopy.**
- **This study highlights the significant effect of leaf wetness formation and evaporation on NH_3 emission and deposition.**

Dry deposition of particles to canopies

Collaboration with Mr. Bruce Hicks: MetCorps (Norris, TN) & Dr. Jonathan Pleim: U.S. EPA (Durham, NC)

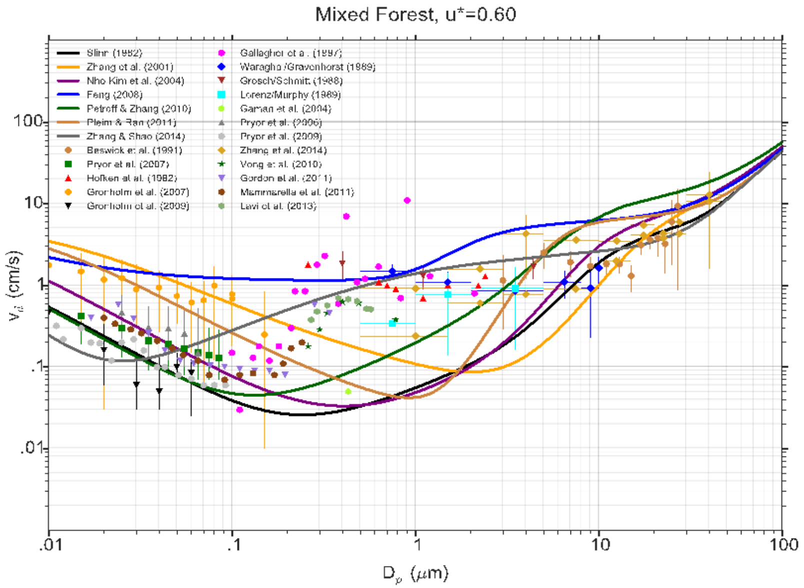
Objective: Estimate how significant the uncertainties in particle deposition algorithms may be in an air quality model's predictions of ground-level fine particle concentrations, particle deposition and total deposition of nitrogen and sulfur.

Air quality model: CAMx, version 6.0, 4-km horizontal resolution.

Model Domain: Southeast U.S.

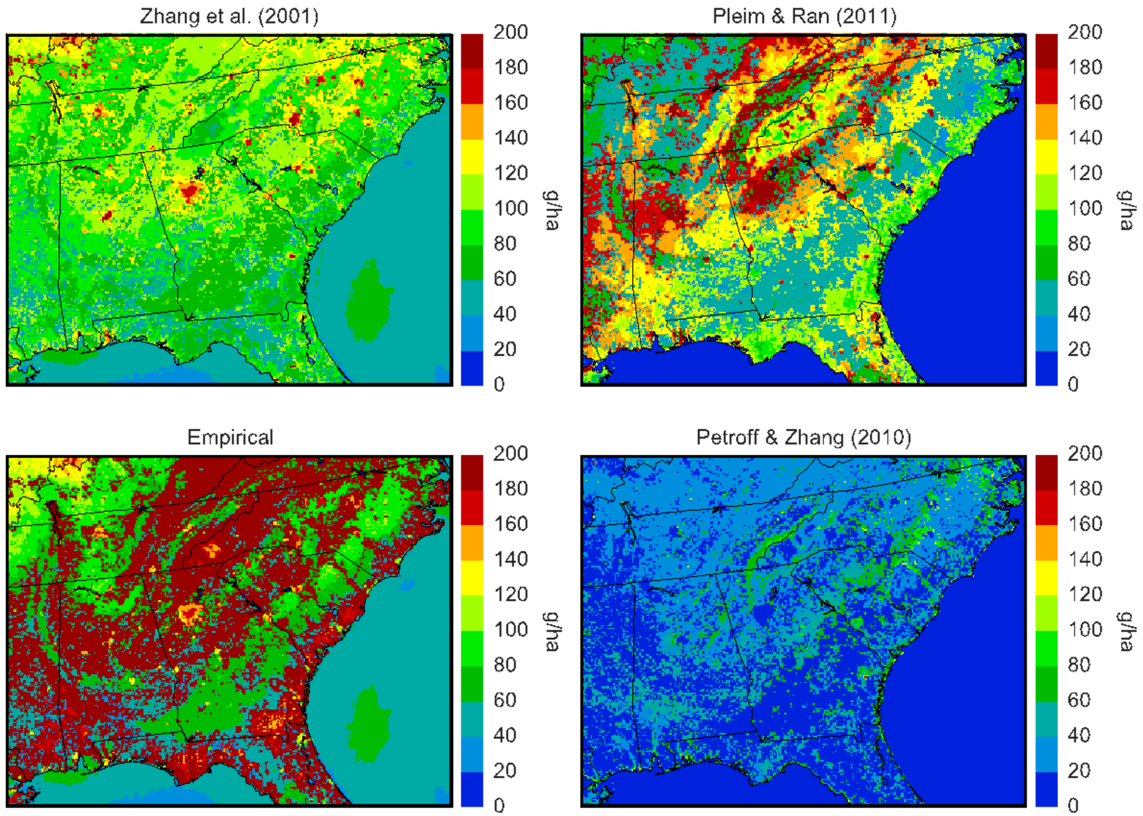
Simulation period: June 14 – 28, 2013.

Model simulations: 2018 - 2019



Divergence of measurements and models for forest canopies

Dry Deposition $PM_{2.5}$



- **Particle dry deposition is a significant uncertainty in air quality models and different algorithms lead to large deposition differences.**
- **This study is leading to a new particle dry deposition scheme being implemented in the Community Multiscale Air Quality (CMAQ) model.**

Quality and Performance: Publications 13

- Lichiheb N., Heuer M., Hicks B. B., Saylor R., Vargas R., Vazquez Lule A., St. Laurent K. and Myles L., (2021). Atmospheric ammonia measurements over a coastal salt marsh ecosystem along the Mid-Atlantic U.S. Journal of Geophysical Research: Biogeosciences, 126, e2019JG005522.
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- Lichiheb N., Myles L., Personne E., Heuer H., Buban M., Nelson A.J., Koloutsou-Vakakis S., Rood M.J., Joo E., Miller J. and Bernacchi C., (2019). Implementation of the effect of urease inhibitor on ammonia emissions following urea-based fertilizer application at a Zea mays field in central Illinois: A study with SURFATM-NH3 model. Agricultural and Forest Meteorology 269-270: 78-87.
- Saylor, R. D.; Baker, B. D.; Lee, P.; Tong, D.; Pan, L.; and Hicks, B. B. (2019). The particle dry deposition component of total deposition from air quality models: right, wrong or uncertain? Tellus B: Chemical and Physical Meteorology, 71(1), 1-22.
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- Nelson A. J., Lichiheb N., Koloutsou-Vakakis S., Rood M. J., Heuer M., Myles L., Joo E., Miller J. and Bernacchi C., (2018). Ammonia flux measurements above a corn canopy using relaxed eddy accumulation and a flux gradient system. Agricultural and Forest Meteorology 264: 104-113.
- Lee, P.; Saylor, R.; and McQueen, J. (2018). Air Quality monitoring and forecasting. Atmosphere, 9(3), 89.
- Balasubramanian, S., A. Nelson, S. Koloutsou-Vakakis, J. Lin, M.J. Rood, L. Myles, and C. Bernacchi. (2017) Evaluation of DeNitrification DeComposition Model for Estimating Ammonia Fluxes from Chemical Fertilizer Application. Agricultural and Forest Meteorology, 237, 123-134.
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- Hicks, B. B., R. D. Saylor, and B. D. Baker (2016). Dry deposition of particles to canopies—A look back and the road forward, Journal of Geophysical Research Atmospheres, 121.
- Saylor, R. D. and B. B. Hicks (2016). New directions: Time for a new approach to modeling surface-atmosphere exchanges in air quality models? Atmospheric Environment 129: 229-233.

Quality and Performance

Presentations (21)

- Lichiheb N, Personne E, Walker J.T, Wu Z, Chen X, Oishi A.C, and Myles, L. (2022). Modeling bi-directional exchanges of NH_3 over a deciduous forest canopy: A study with SURFATM-NH_3 model. AMS. Houston, TX.
- Saylor R, Wu Z, Walker J .T, Chen X, and Oishi C. (2022). Dynamic NH_3 Exchange within a Deciduous Forest Canopy in the Southern Appalachians. AMS. Houston, TX.
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- Hicks B, Lichiheb N, O'Dell D.L., Oetting J., Eash N., Myles L, Heuer M., (2019). Trace gas effluxes at night – the virtual chamber statistical methodology. AGU. San Francisco, CA.
- Lichiheb N, Mark Heuer M, Myles L, Hicks B.B, Saylor R, Vargas R, Vázquez-Lule A, and St. Laurent K., (2019). Atmospheric ammonia measurements over a coastal salt marsh ecosystem along the Mid-Atlantic U.S. AGU. San Francisco, CA.
- Lichiheb N, Heuer M, Vargas R, Vázquez-Lule A, St. Laurent K, Senn D, Klemenz S, Hahn C, Saylor R, and Myles L. (2018). Measurements of nitrogen and carbon fluxes over coastal salt marsh ecosystem in the northeastern U.S. using eddy covariance systems. AGU. Washington, D.C.
- Lichiheb N., (2018). Measuring atmospheric carbon and nitrogen fluxes over coastal salt marsh. *Delaware National Estuarine Research Reserve. St Jones reserve. Delaware*.
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Quality and Performance

Presentations (continued)

- Myles L, Lichiheb N, Heuer M, Buban M, Nelson A.J, Koloutsou-Vakakis S, Rood M.J. (2017). Investigating the processes of ammonia exchanges between the atmosphere and a corn canopy following Urea Ammonium Nitrate (UAN) fertilization with urease inhibitor NBPT. AGU. New Orleans, LA.
- Nelson A, Koloutsou-Vakakis S, Rood M.J., Lichiheb N, Heuer M, Myles L., (2017). Inter-comparison of Flux-Gradient and Relaxed Eddy Accumulation Methods for measuring Ammonia Flux above a corn canopy in central Illinois, USA. AGU. New Orleans, LA.
- Lichiheb N, (2017). Evaluation of ammonia air-surface exchange at the field scale using SURFATM-NH_3 model. University of Tennessee, Knoxville, TN.
- Lichiheb N, Myles L, Personne E, Heuer M, Buban M. (2017). Evaluation of ammonia air-surface exchange at the field scale: Improvement of soil and stomatal emission potential parameterizations. NADP. San Diego, CA.
- Saylor R. , Myles L. , Lichiheb N., Heuer M., Nelson A , Koloutsou-Vakakis S and Rood M. (2017). The Atmospheric Chemistry and Canopy Exchange Simulation System for Ammonia (ACCESS-NH3): Formulation and Application to a Corn Canopy. NADP. San Diego, CA.
- Lichiheb N, (2017). Understanding and evaluating the bi-directional exchanges of ammonia and pesticides applied at the field scale using measurements and modelling approaches, University of Illinois at Urbana-Champaign, Urbana, IL.
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- Balasubramanian, S., A. Nelson, S. Koloutsou-Vakakis, Lin J, L. Myles M.J. Rood. (2016). Evaluation of DeNitrification DeComposition Model to Estimate Ammonia Fluxes from Chemical Fertilizer Application. AGU. San Francisco, CA.
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Future plans

Experimental approach

- Initiate collaboration with Dr. John Walker (U.S. EPA) and scientists from Colorado State University to conduct chemical flux/deposition measurements at Chestnut ridge site.
- Explore the factors that affect litter emissions of NH_3 in agricultural and forest ecosystems.
- Develop micrometeorological techniques to accurately measure NH_3 fluxes in complex terrain (e.g. wetland ecosystems).
- Long-term real-time atmospheric NH_3 concentration measurements to assess the seasonal variability and understand the Nitrogen dynamics in wetlands.
- Detect NH_3 plumes during wildfires using small drones/air crafts.

Modeling approach

- Provide a better estimate of Nr emissions from wildfire plumes and assess the effect of these emissions on Nr deposition downwind from Western U. S. Wildfires.
- Compare multilayer model with big-leaf model results to propose improvements in the existing parameterizations.
- Implement a parameterization describing the dew formation and evaporation processes.
- Develop a parameterization to account for NH_3 emission processes in litter layer.
- Develop a Large Eddy Simulation (LES) capability to better represent exchange processes.

Pilot field study at the St Jones Reserve (Dover, DE)