Processes of ammonia surface-atmosphere exchange in different ecosystems across the U.S

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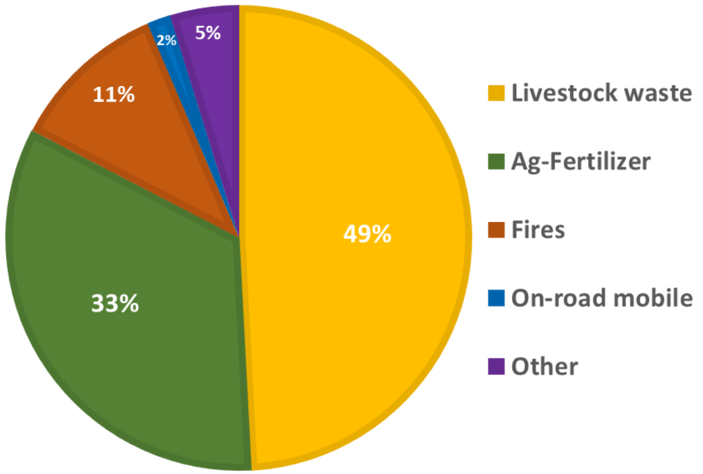
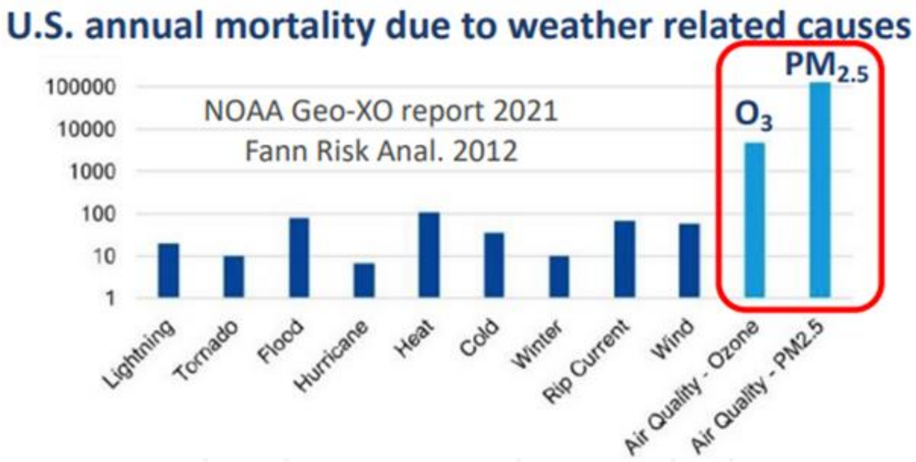
Background: Atmospheric ammonia (NH_3)

- 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:
  - 82 % of all U.S. NH_3 emissions derive from the agricultural sector (US EPA, 2020);
  - Fires account for 11% , mobile source account for 2% of NH_3 emissions in the U.S (US EPA, 2020)… .





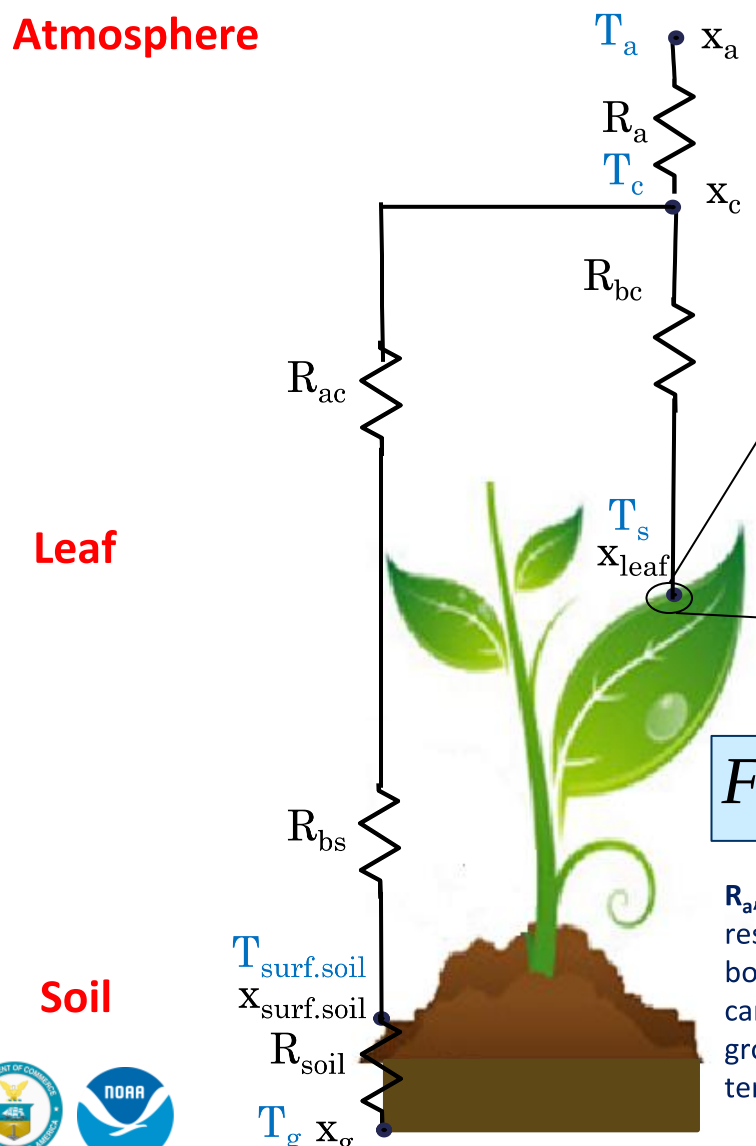
- NH_3 participates in the formation and growth of $PM_{2.5}$.
- Air Quality is a costly and deadly issue affecting millions of people in the U.S. and billions globally.

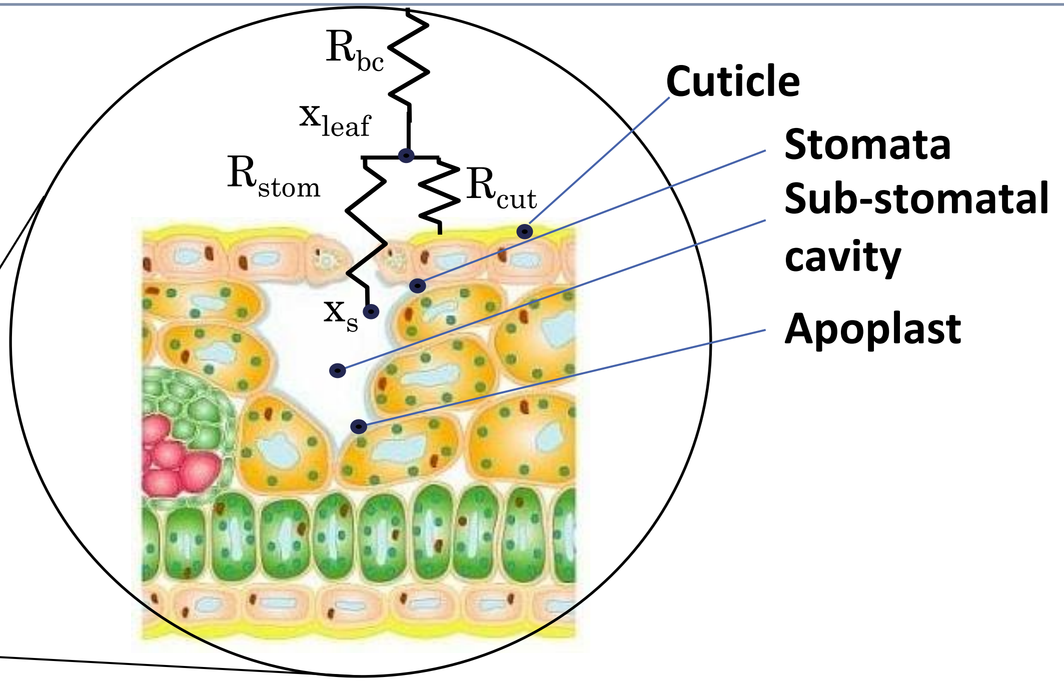
The monitoring of atmospheric NH_3 remains limited. Large uncertainties in model forecasts.

The goal is to explore the future directions of air-surface exchange modeling for NH_3 and the measurements needed to facilitate model improvements.

Two-layer NH_3 compensation point model: SURFATM-NH_3 (Personne et al., 2009)

Collaboration with UMR ECOSYS AgroParisTech-INRAE (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.

Two-layer NH_3 compensation point model: SURFATM-NH_3 (Personne et al., 2009)

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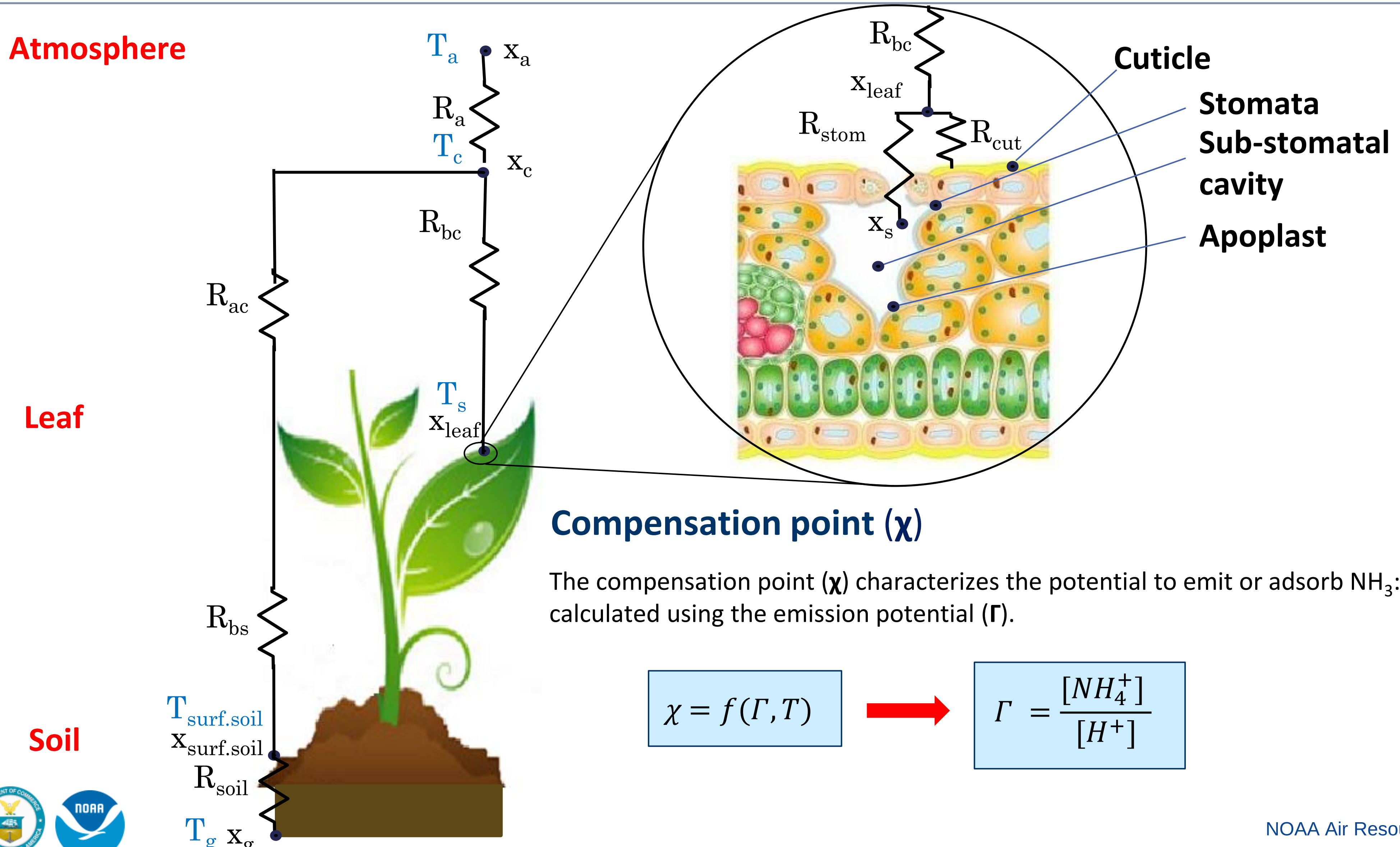

Compensation point (χ)

The compensation point (**χ**) characterizes the potential to emit or adsorb NH_3: calculated using the emission potential (**Γ**).

$$\chi = f(\Gamma, T) \rightarrow \Gamma = \frac{[NH_4^+]}{[H^+]}$$

NH_3 exchanges over an agricultural ecosystem

Collaboration with 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

Fertilizer: Urea Ammonium Nitrate with Urease inhibitor injected to a depth of 10 cm on May 6, 2014 (DOY 126).

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REA sampling system

Relaxed Eddy Accumulation (REA)

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

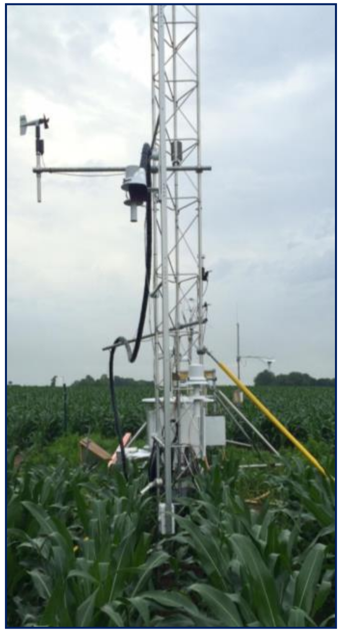
$$\overline{F_{REA}} = \beta \sigma_w \left(\overline{C^{\uparrow}} - \overline{C^{\downarrow}} \right)$$

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

Flux-gradient (FG)

<u>Concept:</u> determines emission and deposition fluxes from vertical gradient of air concentrations.

$$F_{FG} = -K_H \left(\frac{\Delta C_{NH_3}}{\Delta z} \right) = F_H \left(\frac{\Delta C_{NH_3}}{\Delta T} \right)$$

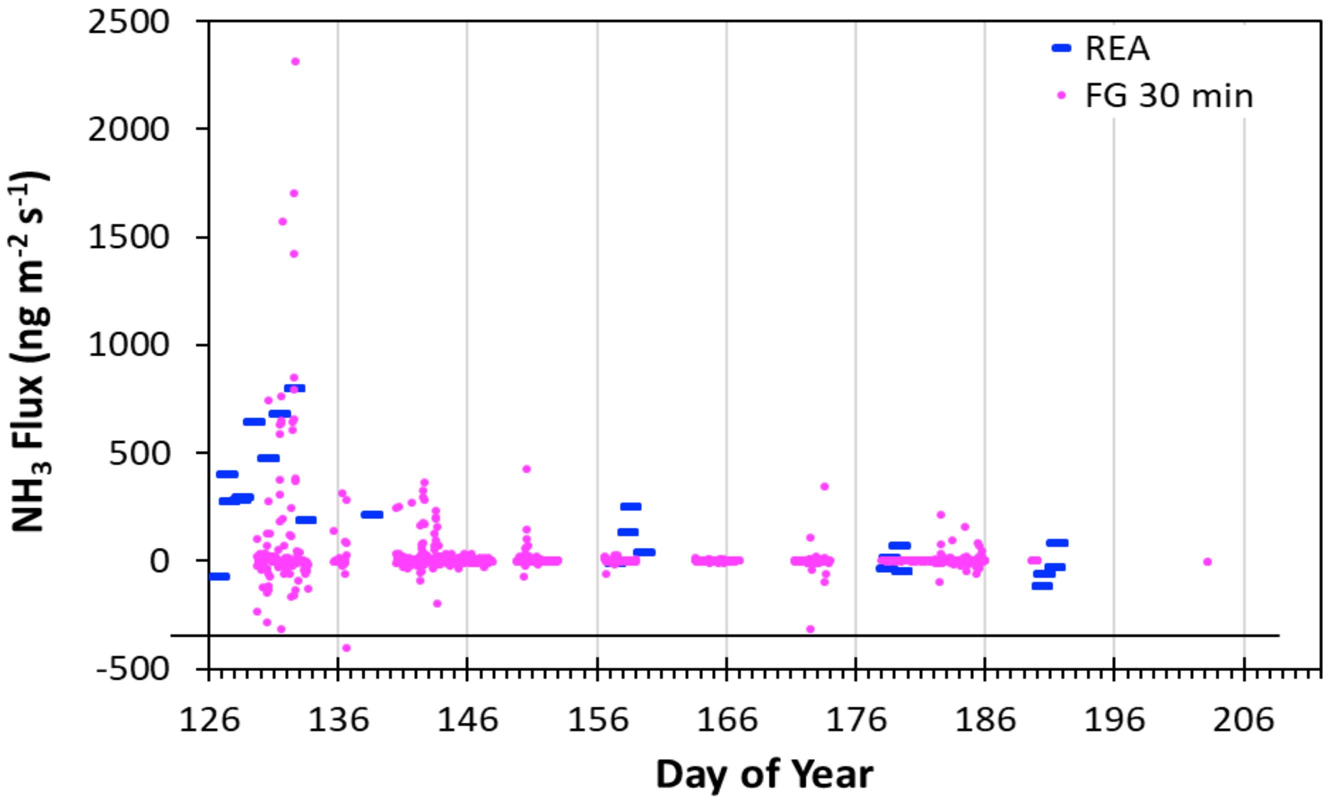


FG sampling system

$\boldsymbol{F_{FG}}$ is the flux from FG, $\boldsymbol{K_H}$ is the eddy diffusivity for sensible heat, $\boldsymbol{\Delta C_{NH3}}$ is the difference in NH_3 concentration between two measurement heights (**Δ*z***), **Δ*T*** is the corresponding difference in temperature.

NH_3 exchanges over an agricultural ecosystem

➢ Results



NH_3 fluxes measured using REA and FG techniques
(Nelson, et al., 2019)

➡ The FG technique enabled high temporal resolution of NH_3 fluxes: the detection of the NH_3 peak just after the fertilization, the detection of deposition fluxes.

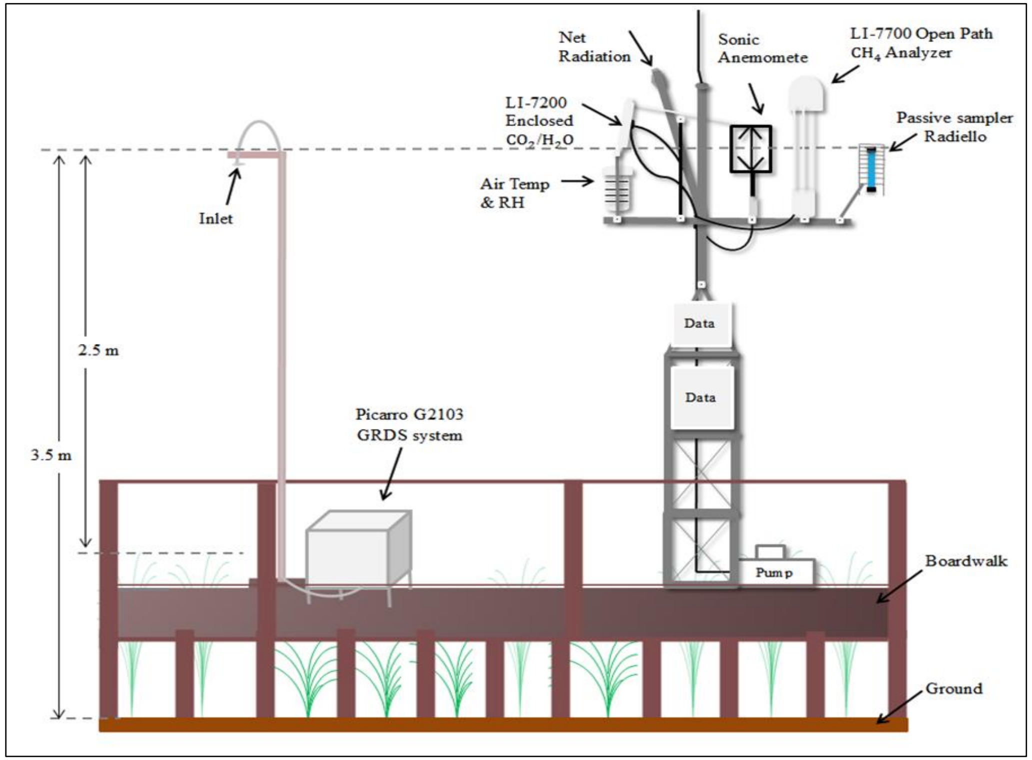
Atmospheric NH_3 measurements over a coastal ecosystem

Collaboration with Delaware National Estuarine Research Reserve (Dover, DE) & 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.



Schematic of the experimental set-up

CRDS system

Radiello passive sampler

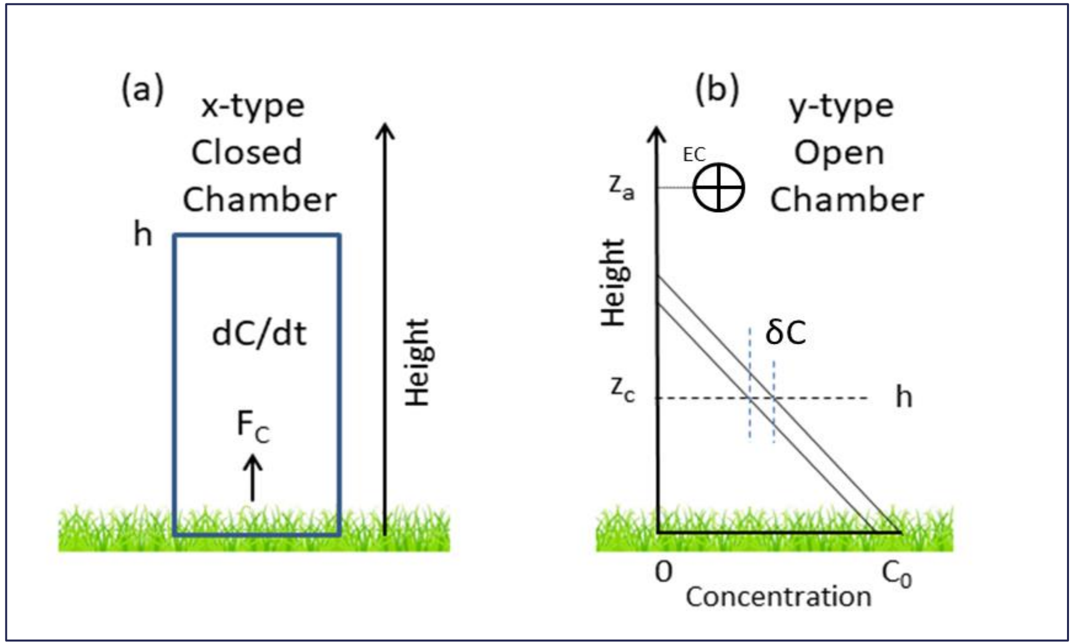
- Continuous NH_3 concentrations were measured with Cavity Ringdown Spectroscopy (CRDS) system.
- A week-long sampling period of NH_3 concentration measurements by passive samplers (AMoN, National Atmospheric Deposition Program).
- Meteorological measurements provided from the St. Jones Ameriflux site (US-StJ) hosted by the University of Delaware.

The virtual chamber statistical concept (Hicks et al., 2021)

Collaboration with 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.



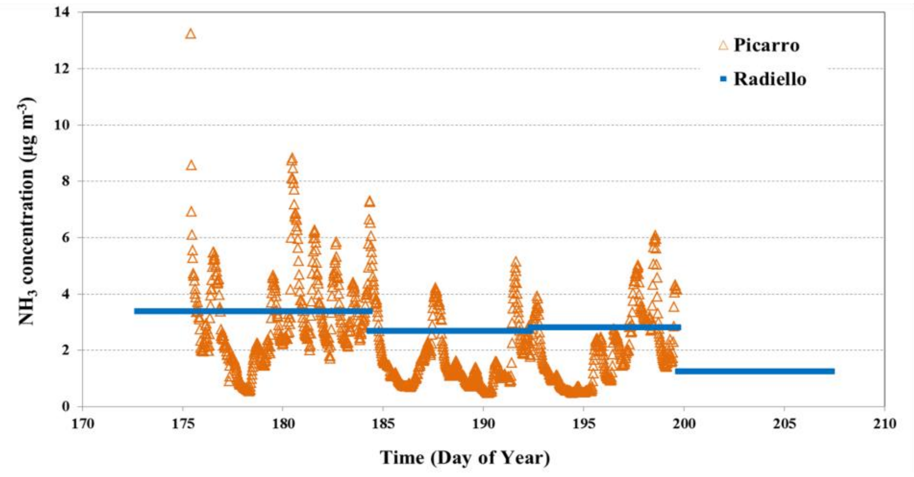
Schematic illustrations of the virtual chamber method

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**).

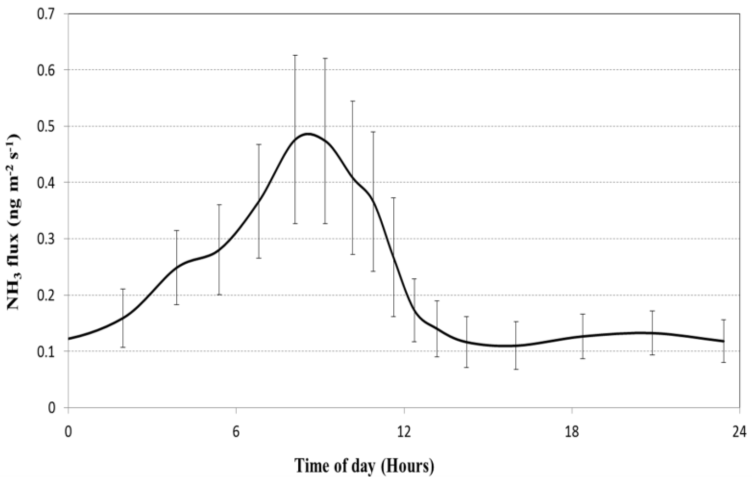
$$F_{NH_3} = C_{NH_3} h(u/x)$$

Atmospheric NH_3 measurements over a coastal ecosystem

- **Results** (Lichiheb et al., 2021)

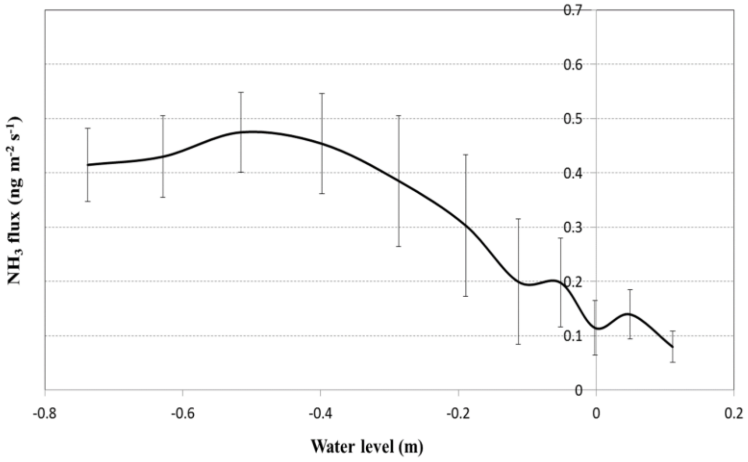


NH_3 concentrations measured using the CRDS and the passive Radiello samplers



Average diurnal cycle of NH_3 fluxes as a function of time

- Tidal depths have a significant effect on NH_3 emissions: the highest NH_3 fluxes were observed at low tide when more soil/island was exposed.
- Salt marshes could be a sink of NH_3 via atmospheric deposition or a source of NH_3 in anaerobic and aerobic conditions.



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

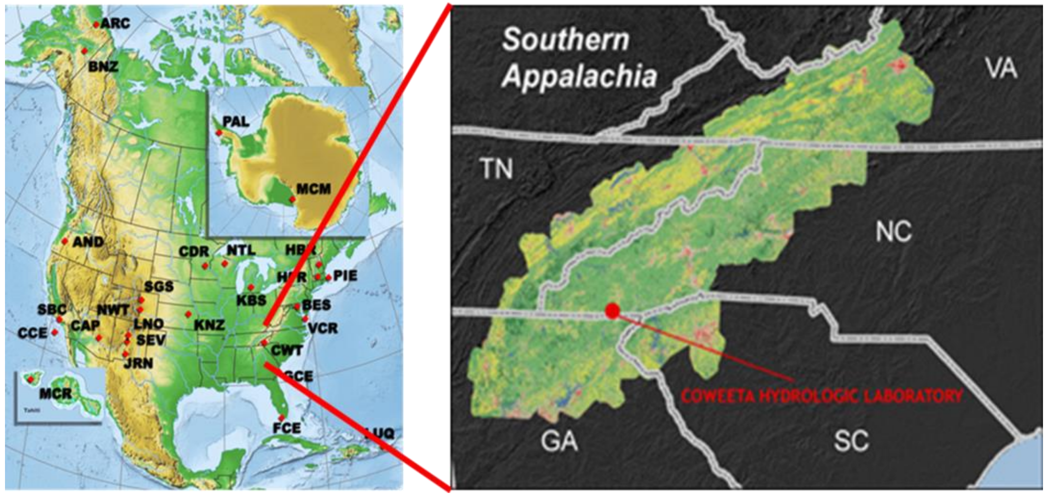
Bi-directional exchanges of NH_3 over a deciduous forest canopy

Collaboration with 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.

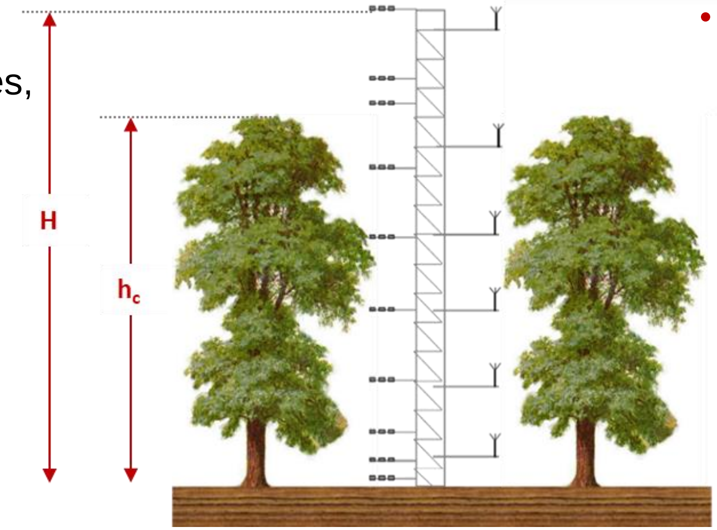
Study period: From May 21 - June 9, 2015; August 6 – 25, 2015; September 9 – 26, 2015; April 19 – May 11, 2016; and July 13 – August 3, 2016.



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.

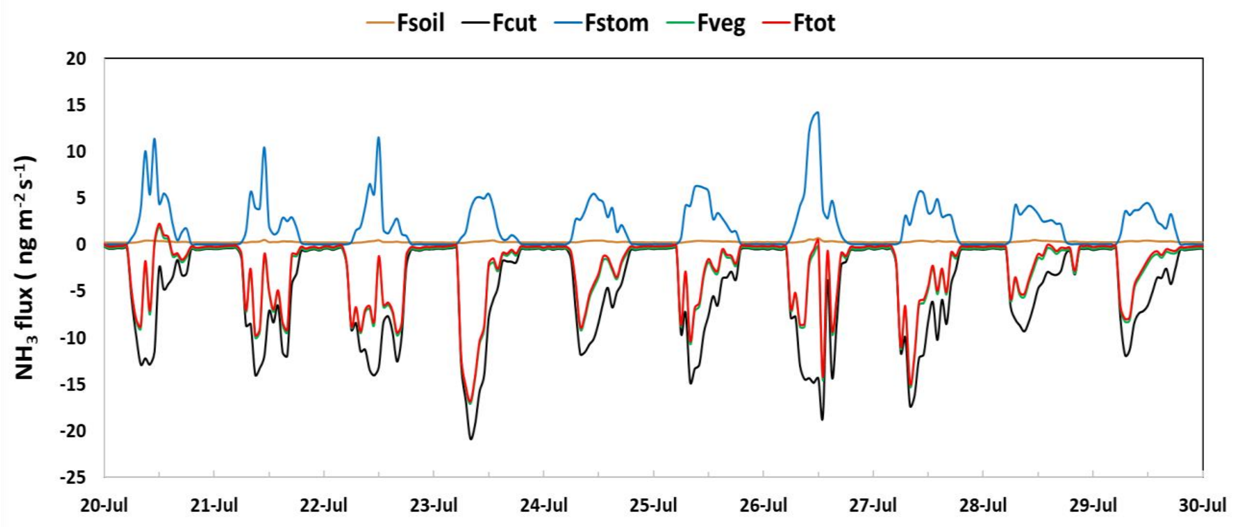


Eddy Flux Tower

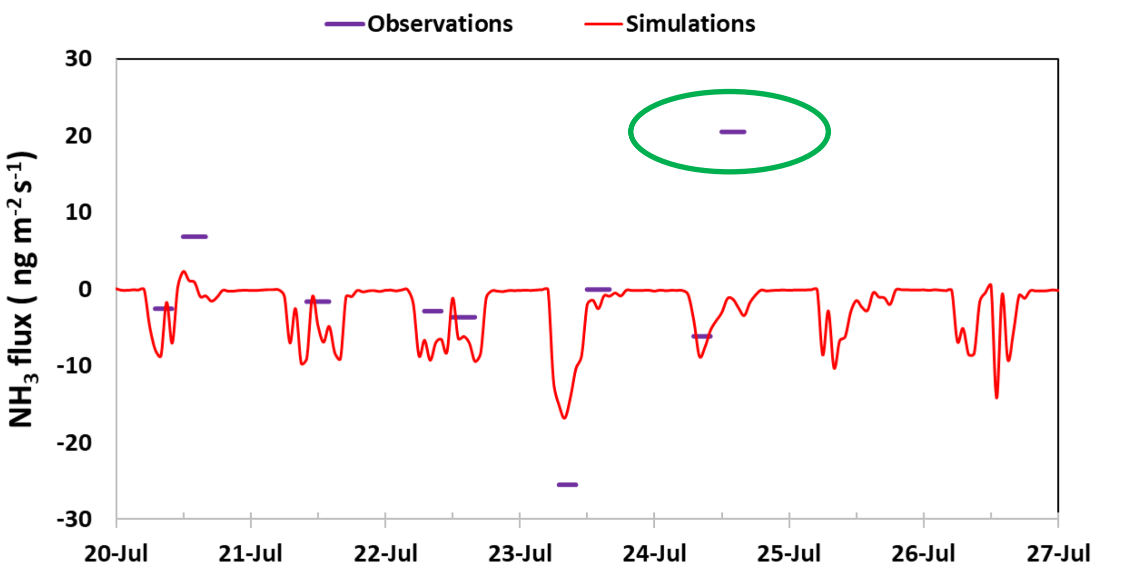
- **Initialization of SURFATM-NH_3 model**
  - **Canopy height:** h_c=35m
  - **Measurement height**: H= 43 m
  - **Total canopy LAI** = 4.6
  - **Initial focus:** July 20-30, 2016
  - **Measured NH_3 concentrations:** denuder and MARGA
  - **Implemented emission potentials (Γ):**
    - Stomatal emission potential: Γ_s = 40
    - Ground/Litter emission potential: Γ_g =200

Bi-directional exchanges of NH_3 over a deciduous forest canopy

➢ Results



Simulation of the different sources of NH_3 fluxes with SURFATM-NH_3 model

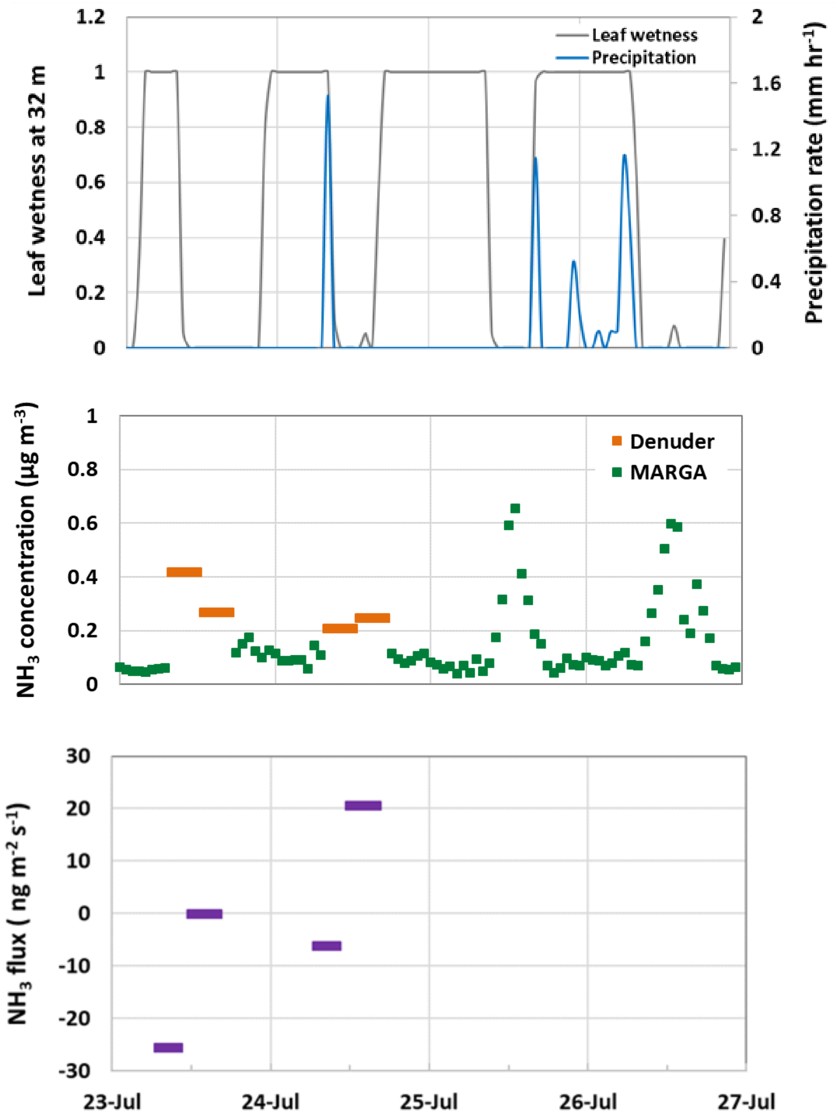


Comparison of measured and modeled NH_3 fluxes

- Dominance of the cuticular pathway, resulting in only deposition fluxes during almost the whole study period.
- SURFATM-NH_3 can reasonably reproduce NH_3 deposition fluxes.
- Measured NH_3 emission fluxes during specific meteorological conditions are not well reproduced by the model.

Bi-directional exchanges of NH_3 over a deciduous forest canopy

➢ Effect of leaf wetness formation and evaporation



- The evaporation of leaf surface wetness (dew droplets/rain) in the morning leads to higher NH_3 air concentrations.
- There is a striking dependence on the wetting source of the leaf surface. The higher emission flux (20.5 ng m^{-2} s^{-1}) occurred after a rain event (1.5 mm) on July 24^{th}.
- Dew pH is generally higher than rain pH. The decreased pH caused by rain increases NH_3 uptake by leaf surface water. This led to a high emission flux of NH_3 after complete dryness of the leaf surface water film.

➡ **Understanding the role of leaf surface adsorption and desorption processes is fundamental to better describe the processes of bi-directional NH_3 exchange.**

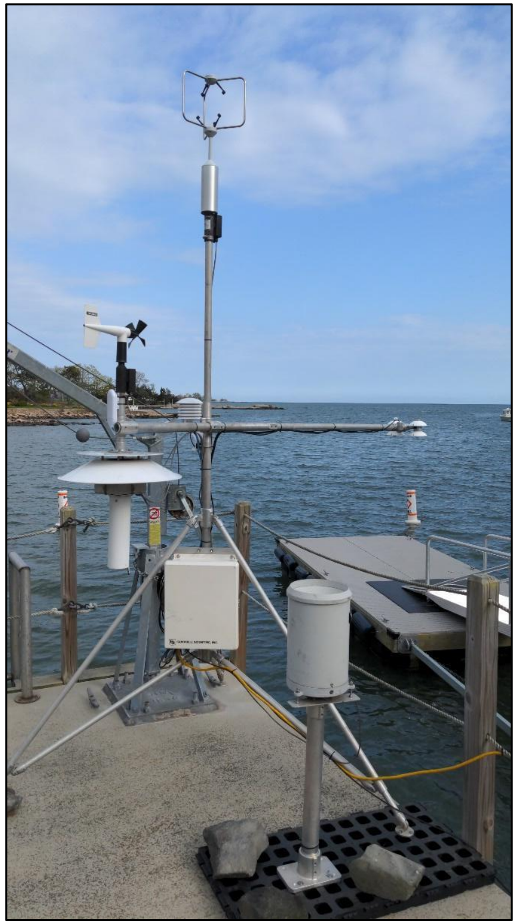
Spatial and temporal NH_3 variations in urban and suburban areas

Collaboration with Yale University and Princeton University

NOAA ARL mobile measurement platform

- Ongoing NH_3 concentration measurements within the **A**tmospheric **E**missions and **R**eactions **O**bserved from **M**egacities to **M**arine **A**rea (AEROMMA) campaign.
- On-road NH_3 concentrations using a mobile platform including an open-path NH_3 sensor in NYC and at the Yale Coastal Field Station (YCFS) (Guilford, CT).
- Ground- based measurements using the CRDS system (G2103, Picarro) at the (YCFS) (Guilford, CT).

Experimental setup of the open-path NH_3 sensor on the mobile platform at Princeton University



Meteorological tower mounted on the boardwalk at the YCFS

Future work

- Analyze the long-term real-time atmospheric NH_3 concentration measurements collected at the YCFS to assess the seasonal variability and understand the Nitrogen dynamics in wetlands.
- Analyze the on-road NH_3 concentration measurements to better understand the spatial and temporal NH_3 variations in urban and suburban areas, and to calculate NH_3 emission factors (EF).
- Develop micrometeorological techniques to accurately measure NH_3 fluxes in complex terrain (e.g. wetland ecosystems).
- Adapt SURFATM-NH_3 model in order to describe the exchange of NH_3 between the atmosphere and the aquatic surface in coastal ecosystems: develop a coastal biogeochemical (CBG) model and validate it using field measurements obtained in this project.
- Implement a parameterization describing the dew formation and evaporation processes.
- Compare multilayer model with big-leaf model results to propose improvements in the existing parameterizations.

Thank you for your attention

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