Atmospheric ammonia measurements over a coastal salt marsh ecosystem along the Mid-Atlantic U.S.

Nebila Lichiheb[1], Mark Heuer[1,2], Bruce B. Hicks[3], Rick Saylor[1], Rodrigo Vargas[4], Alma Vázquez-Lule[4], Kari St. Laurent[5], and LaToya Myles[1]

*Nebila.Lichiheb@noaa.gov

Context & Objective

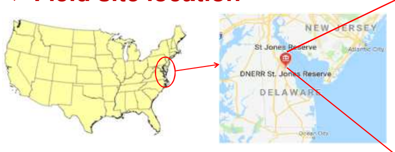
Coastal wetlands such as salt marshes, seagrasses, and mangroves provide an optimum natural environment for the sequestration and long-term storage of carbon (C) from the atmosphere, commonly known as coastal blue carbon. There are over 4 million acres of salt marsh in the US and over half of these marshes are along the Atlantic Coast. Due to anthropogenic activities, a growing nitrogen (N) pollution problem exists in coastal ecosystems from atmospheric N deposition, runoff, and riverine export. Despite this, there are limited atmospheric measurements of ammonia (NH_3) concentrations and fluxes in coastal areas of the Eastern and Mid-Atlantic U.S.

The purpose of this study is to advance our process-level understanding of NH_3 air-surface exchange over a coastal salt marsh along the Mid-Atlantic U.S. The pilot study presented here represents one of the few atmospheric measurements of NH_3 over a tidal salt marsh in the Mid-Atlantic U.S.

Materials and Methods

- Continuous and high-temporal resolution measurements of atmospheric NH_3 concentrations in the St Jones Reserve component of the Delaware National Estuarine Research Reserve from 21 June to 20 July 2018.
- Soil, plant and water chemistry analysis.
- Estimation of the average diurnal cycle of NH_3 fluxes.

❖ Field site location



- 15 replicates of sediments were collected on DOY 200 at 0-5 cm of depth with 20 g of soil/sample.
- 15 replicates of plants (*Spartina alterniflora*) were collected on DOY 180 and 200 with 30 g of plant/sample.
- Water samples were collected on DOY 197 from the St. Jones Reserve tidal creek at the Scotton Landing station.

Figure 1: Sampling zone of soil and plants within the 200 m radius from the eddy covariance (EC) tower

❖ NH_3 concentrations & meteorological measurements

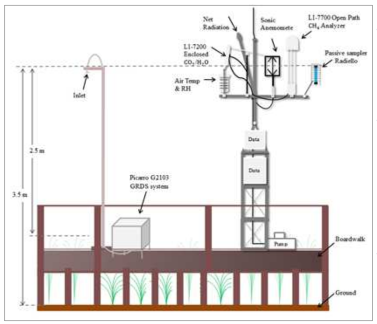


Figure 2: Schematic of the EC tower, the Radiello and the CRDS system

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

❖ Estimation of the average diurnal cycle of NH_3 fluxes

The analytical method presented by ***Hicks et al. (2019)*** has been adapted to derive the average diurnal cycle of NH_3 fluxes by considering the study site as a virtual chamber. 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**).

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

Results

Table 1: Summary of total N, NH_4^+ and nitrate (NO_3^-) concentrations, along with pH from plant, soil and water sampled during the experimental study.

Sampling day		Plant	Soil	Water
DOY 180	Total N (mg kg^{-1})	9833.33 ± 1237.89	-	-
	NH_4^+ (mg kg^{-1})	763.47 ± 351.59	-	-
	pH	6.09 ± 0.15	-	-
DOY 197	NH_4^+ (mg L^{-1})	-	-	0.07 ± 0.02
	NO_3^- (mg L^{-1})	-	-	0.08 ± 0.02
	pH	-	-	7.40 ± 0.32
DOY 200	Total N (mg kg^{-1})	7066.67 ± 1272.04	6425.00 ± 2194.39	-
	NH_4^+ (mg kg^{-1})	416.53 ± 104.36	41.73 ± 18.87	-
	NO_3^- (mg kg^{-1})	-	0.24 ± 0.15	-
	pH	5.99 ± 0.10	6.67 ± 0.32	-

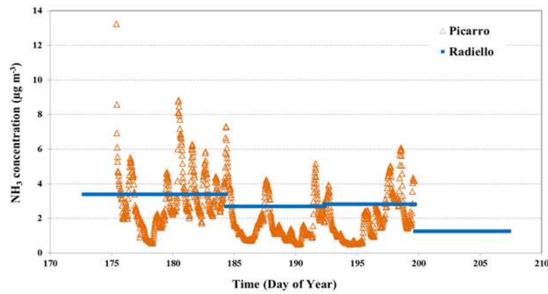


Figure 3: NH_3 concentrations as measured using the CRDS and the passive Radiello samplers at the St Jones reserve site.

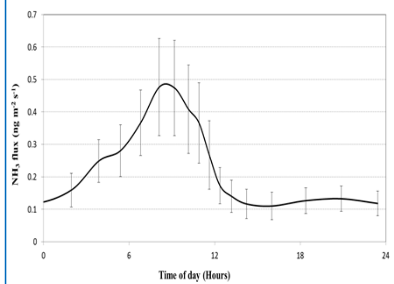


Figure 4: Average diurnal cycle of NH_3 fluxes as a function of time.

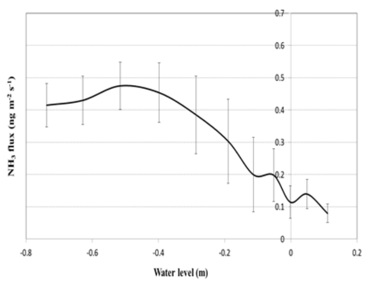


Figure 5: Average diurnal cycle of NH_3 fluxes as a function of tidal depth.

Discussion

❖ NH_3 concentrations

- Continuous NH_3 concentrations from the CRDS are reported as 30 min averages; passive sampling occurred over a week-long sampling period.
- Mean and standard deviation values of NH_3 concentration from the CRDS and the passive Radiello samplers were 2.33 ± 1.54 µg m^{-3} and 2.53 ± 0.9 µg m^{-3}, respectively.
- Both methods gave the same range of measured NH_3 concentrations.
- Measured NH_3 concentration using the CRDS showed a diurnal pattern with two prominent concentration peaks of 13.25 µg m^{-3} and 8.82 µg m^{-3} on DOY 175 and 180, respectively.

The use of the CRDS enabled high temporal resolution measurements of NH_3 concentrations: greater details into the fluctuations of NH_3 concentrations than standard methods.

❖ NH_3 fluxes estimation

- Average diurnal cycle of NH_3 fluxes estimated by the virtual chamber method shows NH_3 emissions starting at sunrise, peaking between 8 and 9 am, then decreasing over time.
- Early decline in NH_3 fluxes may be attributed to the tidal influences on NH_3 emissions.
- Average diurnal cycle of NH_3 fluxes as a function of water level shows that lower water levels are associated with high NH_3 fluxes.
- NH_3 volatilization from aqueous systems is directly related to the concentration of ammoniacal N originating principally from the soil ***(Vlek and Stumpe, 1978)***.
- Salt marshes could be a sink of NH_3 via the atmospheric deposition process or a source of NH_3 in anaerobic and aerobic conditions:
  - ➢ In anaerobic conditions (deep sediments): denitrification process is the major pathway of N removal from wetlands.
  - ➢ In aerobic conditions: NH_3 volatilization is not considered as an important mechanism of N losses from wetlands except where high NH_4^+ concentrations of the water exist in conjunction with high water pH (pH above 7.2) ***(Johnston, 1991)***.

Future Work

- Further continuous measurements of NH_3 concentrations using the CRDS instrument are needed for longer durations and during different seasons.
- Further applications of the new analytical method are needed in a variety of ecosystems.

References

- Hicks, B. B., Lichiheb, N., O'Dell, D.L., Oetting, J., Eash, N.S., Heuer, M., Myles, L. (2019). On surface fluxes at night-the virtual chamber approach. In review.
- Johnston, C. A. (1991). Sediment and nutrient retention by freshwater wetlands: Effects on surface water quality. Critical Reviews in Environmental Control, 21, 491-565.
- Vlek, P. L. G. and Stumpe, J. M. (1978). Effects of Solution Chemistry and Environmental Conditions on Ammonia Volatilization Losses From Aqueous Systems1. Soil Science Society of America Journal, 42, 416-421.

Affiliations

[1]*NOAA Air Resources Laboratory Atmospheric Turbulence and Diffusion Division, Oak Ridge, TN 37831, USA*
[2]*Oak Ridge Associated Universities, Oak Ridge, TN 37830, USA*
[3]*MetCorps, PO Box 1510, Norris, TN 37828, USA*
[4]*Department of Plant & Soil Sciences, University of Delaware, Newark, DE 19716, USA*
[5]*Delaware Department of Natural Resources and Environmental Control, Delaware National Estuarine Research Reserve, Dover, DE 19901, USA*