

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

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November 24, 2022

Abstract

Terrestrial-aquatic interfaces such as salt marshes, mangroves, and similar wetlands 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 are along the east coast of the US. Due to anthropogenic activities, this area presents the greatest nitrogen (N) pollution problem in coastal ecosystems in the U.S. as part of atmospheric N deposition, runoff, and riverine export. Ammonia (NH₃) is the most abundant alkaline gas in the atmosphere. Agricultural intensification is the primary anthropogenic source of NH₃ leading to a doubling of reactive nitrogen (N_r) entering the biosphere. Despite this, there are limited atmospheric measurements of NH₃ concentrations in coastal areas along the east coast. The objective of this study is to advance our process-level understanding of NH₃ air-surface exchange over a tidal salt marsh at the Saint Jones Reserve (DE), which is part of the National Estuarine Research Reserve System (NERRs). Continuous and high temporal resolution measurements of atmospheric NH₃ concentrations were measured using a cavity ring-down spectrometer, reporting 30 min concentration averages. These high temporal resolution measurements allowed the estimation of the average diurnal cycle of NH₃ fluxes using a new analytical methodology. Micrometeorological measurements were also measured using the eddy covariance system operated concurrently above the tidal marsh at the research site, which is part of the AmeriFlux network (US-StJ). This pilot study represents one of the few atmospheric measurements of NH₃ over a tidal salt marsh in the eastern U.S. Such measurements are important to characterize the processes that influence the exchanges of NH₃ between the atmosphere and the aquatic surface and provide baseline data to form more reliable parameterizations to simulate NH₃ deposition and emissions in tidal salt marshes using surface-atmosphere transfer models.

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 (NH₃) 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 NH₃ 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 NH₃ over a tidal salt marsh in the Mid-Atlantic U.S.

Materials and Methods

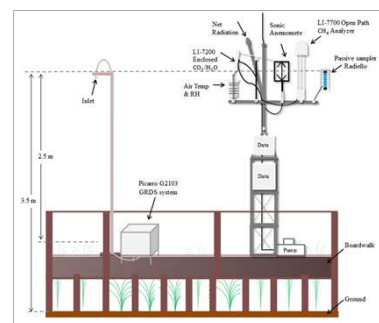
- Continuous and high-temporal resolution measurements of atmospheric NH₃ concentrations in the St Jones Reserve component of the Delaware National Estuarine Research Reserve from 21 June to 20 July 2018.
- Soil, plant and water chemistry analysis.
- Estimation of the average diurnal cycle of NH₃ fluxes.

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.

NH₃ concentrations & meteorological measurements



- Continuous NH₃ concentrations were measured with Cavity Ringdown Spectroscopy (CRDS) system.
- A week-long, integrated sampling of NH₃ 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.

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

Estimation of the average diurnal cycle of NH₃ fluxes

The analytical method presented by Hicks et al. (2019) has been adapted to derive the average diurnal cycle of NH₃ 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 NH₃ (F_{NH₃}) was constant, the concentrations of NH₃ (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, NH₄⁺ and nitrate (NO₃⁻) 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	-

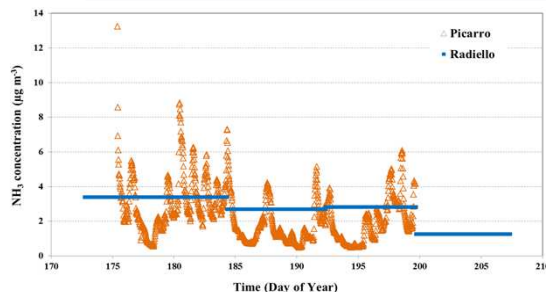


Figure 3: NH₃ concentrations as measured using the CRDS and the passive Radiello samplers at the St Jones reserve site.

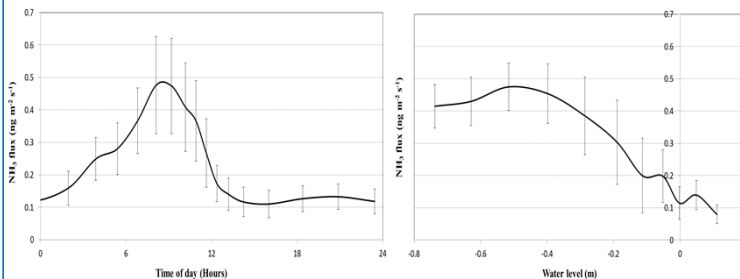


Figure 4: Average diurnal cycle of NH₃ fluxes as a function of time.

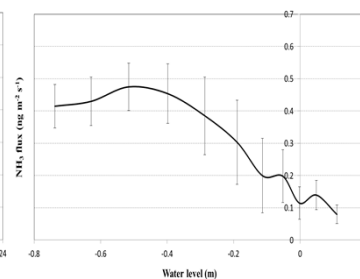


Figure 5: Average diurnal cycle of NH₃ fluxes as a function of tidal depth.

Discussion

NH₃ concentrations

- Continuous NH₃ 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 NH₃ 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 NH₃ concentrations.
- Measured NH₃ 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 NH₃ concentrations: greater details into the fluctuations of NH₃ concentrations than standard methods.

NH₃ fluxes estimation

- Average diurnal cycle of NH₃ fluxes estimated by the virtual chamber method shows NH₃ emissions starting at sunrise, peaking between 8 and 9 am, then decreasing over time.
- Early decline in NH₃ fluxes may be attributed to the tidal influences on NH₃ emissions.
- Average diurnal cycle of NH₃ fluxes as a function of water level shows that lower water levels are associated with high NH₃ fluxes.
- NH₃ volatilization from aqueous systems is directly related to the concentration of ammoniacal N originating principally from the soil (Viek and Stumpe, 1978).
- Salt marshes could be a sink of NH₃ via the atmospheric deposition process or a source of NH₃ in anaerobic and aerobic conditions:
 - In anaerobic conditions (deep sediments): denitrification process is the major pathway of N removal from wetlands.
 - In aerobic conditions: NH₃ volatilization is not considered as an important mechanism of N losses from wetlands except where high NH₄⁺ concentrations of the water exist in conjunction with high water pH (pH above 7.2) (Johnston, 1991).

Future Work

- Further continuous measurements of NH₃ 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.
- Viek, P. L. G. and Stumpe, J. M. (1978). Effects of Solution Chemistry and Environmental Conditions on Ammonia Volatilization Losses From Aqueous Systems. Soil Science Society of America Journal, 42, 416-421.

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