HEALTHY PHOTON

An open-path QCL-based instrument with sub-ppbv sensitivity for eddy covariance measurement of NH_3 fluxes

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BG3.3 "Gas exchange between soil, plants and atmosphere"

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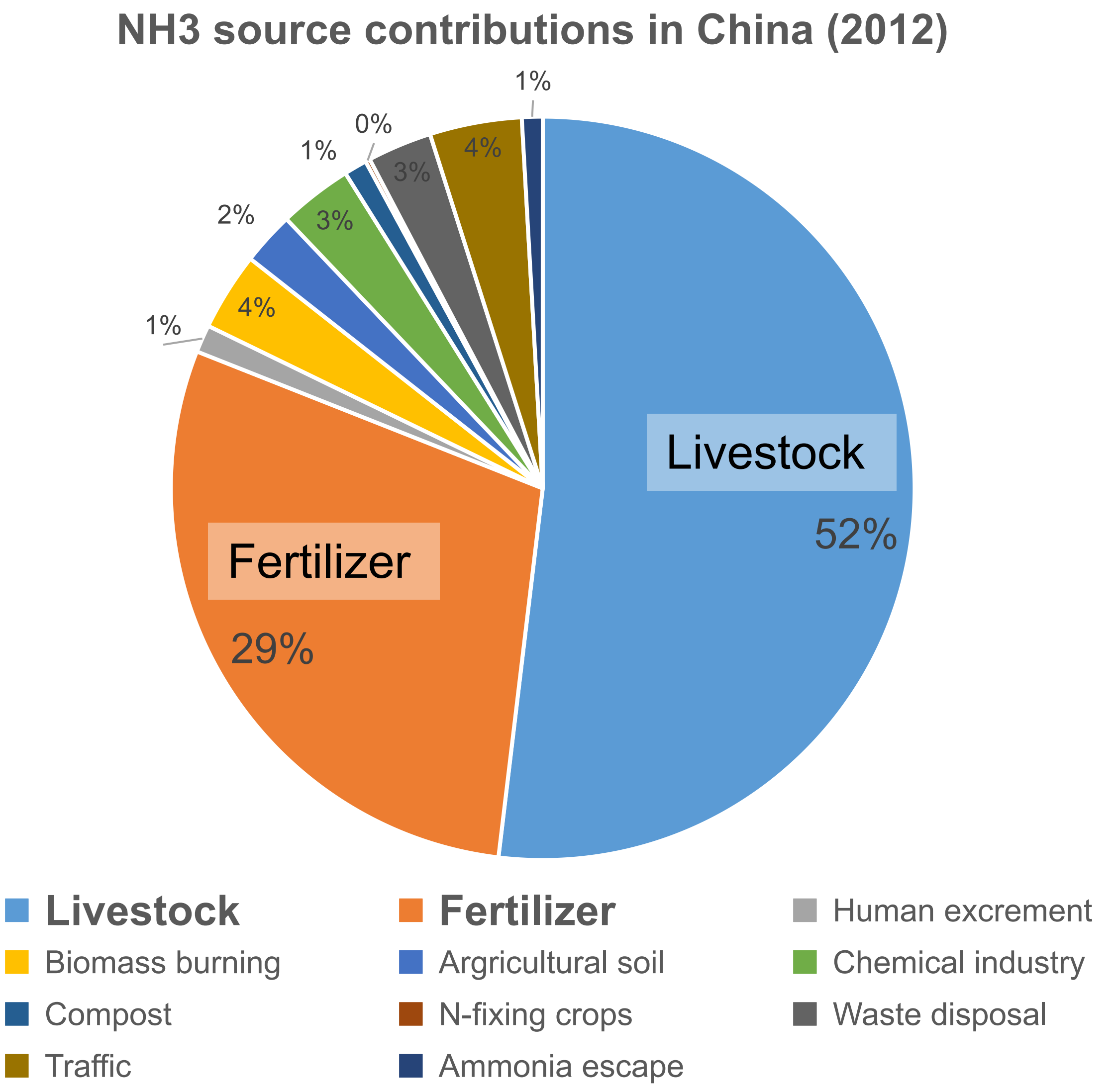
or let's chat on Friday, 8 May 2020, 10:45-12:00AM (CEST), @ EGU2020-6223, online session BG3.3

NH_3 emissions in China

- Ammonia (NH_3): a colorless gas with a pungent odor, very soluble in water, strong adsorption effect
    - a gas-phase precursor to PM2.5
    - form fine particle NH_4+ aerosols

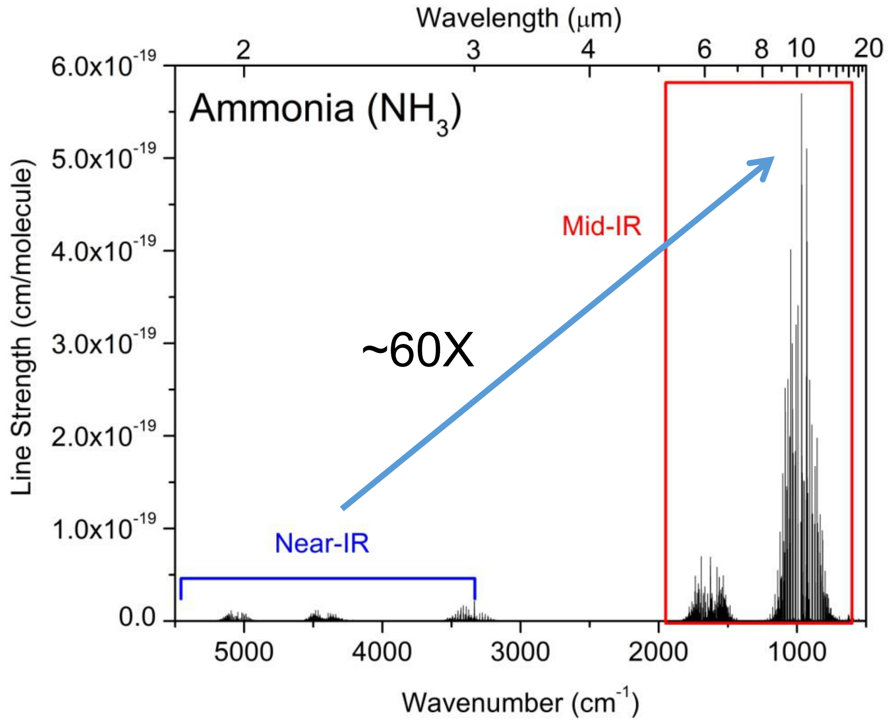


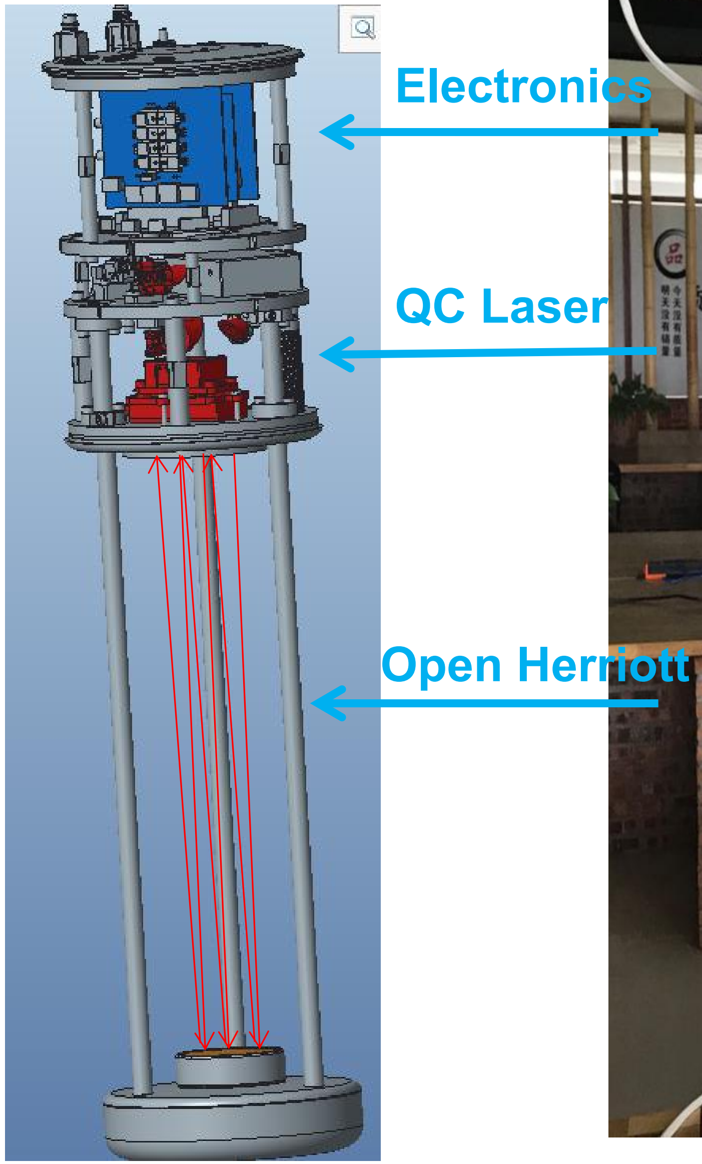
Kang, Y., Liu, M., Song, Y., Huang, X., Yao, H., Cai, X., Zhang, H., Kang, L., Liu, X., Yan, X., He, H., Zhang, Q., Shao, M., and Zhu, T.: High-resolution ammonia emissions inventories in China from 1980 to 2012, Atmos. Chem. Phys., 16, 2043–2058, https://doi.org/10.5194/acp-16-2043-2016, 2016.

Motivation

- **Objective**: To explore the impact of agricultural fertilization on NH_3 emissions/depositions at different ecosystems
- **Methodology**: Eddy covariance technique based on a novel QCL-based open-path trace NH_3 analyzer
- **Requirements**:
  - **High sensitivity** and **high speed** for eddy covariance
  - **Large dynamic range** (before&after fertilization)
  - **Avoid sampling error** due to NH_3 adsorption nature
  - **Low power**
    - Remote sites without readily electrical power
    - Electrical safety problems in the wet rice paddy

Solution: an open-path QCL based NH_3 analyzer



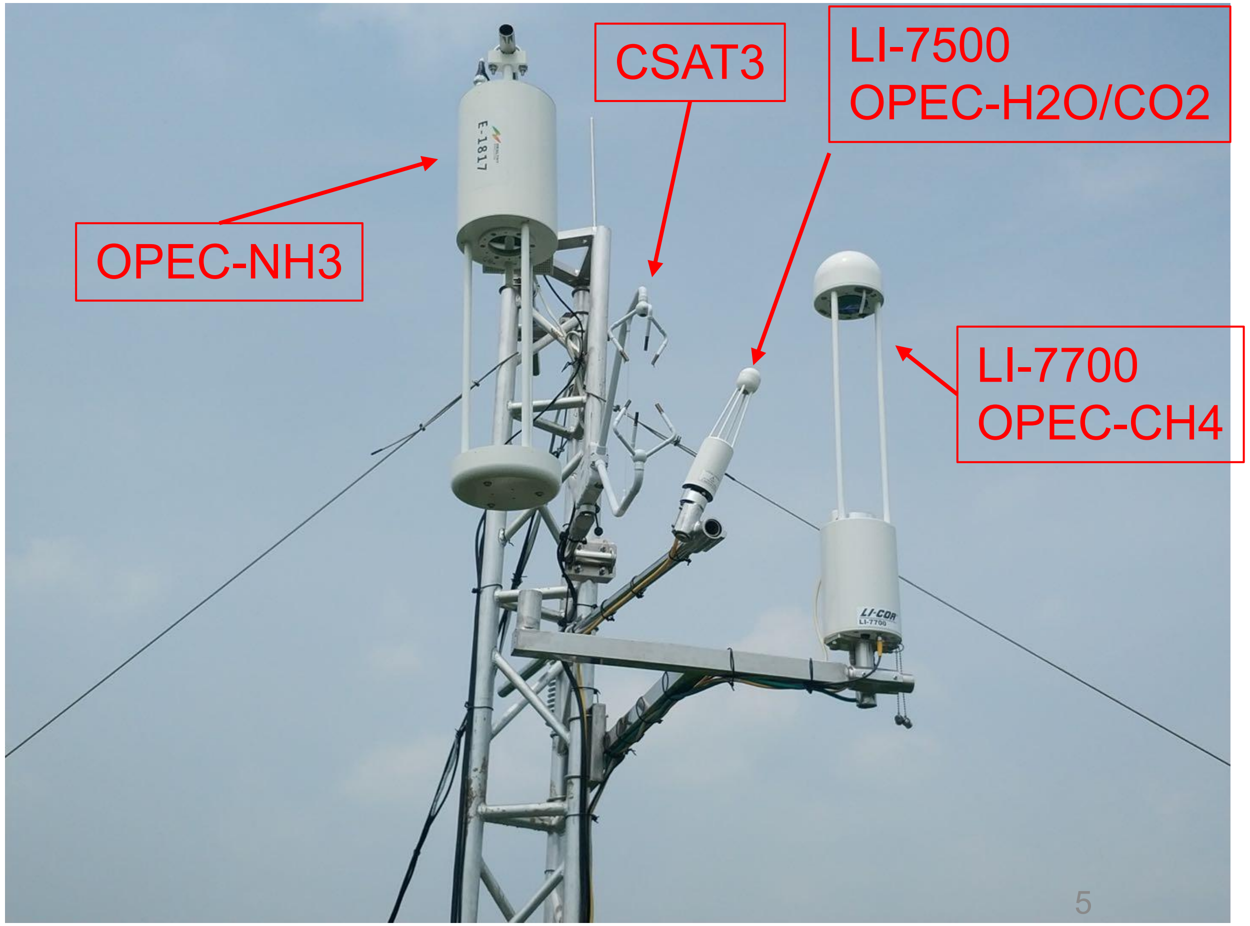


- Strong **mid-infrared** absorber --> high sensitivity
- Distinct absorption lines --> high selectivity
- No consumables --> Unattended continuous monitoring
- **Open-path** --> Fast response, no sampling delay/loss
- No sampling pump and pretreatment --> low power

Miller, D. J., Sun, K., Tao, L., and Zondlo, M. A.: Open-path, quantum cascade-laser-based sensor for high-resolution atmospheric ammonia measurements, Atmos. Meas. Tech., 7, 81–93,2014.

Eddy covariance system

- NH_3 flux system： NH_3 analyzer, Campbell Scientific® CSAT3 + CR6, LICOR® LI-7500
- **Low-power**: Supported by 24VDC solar panels. Safe in wet rice paddy.



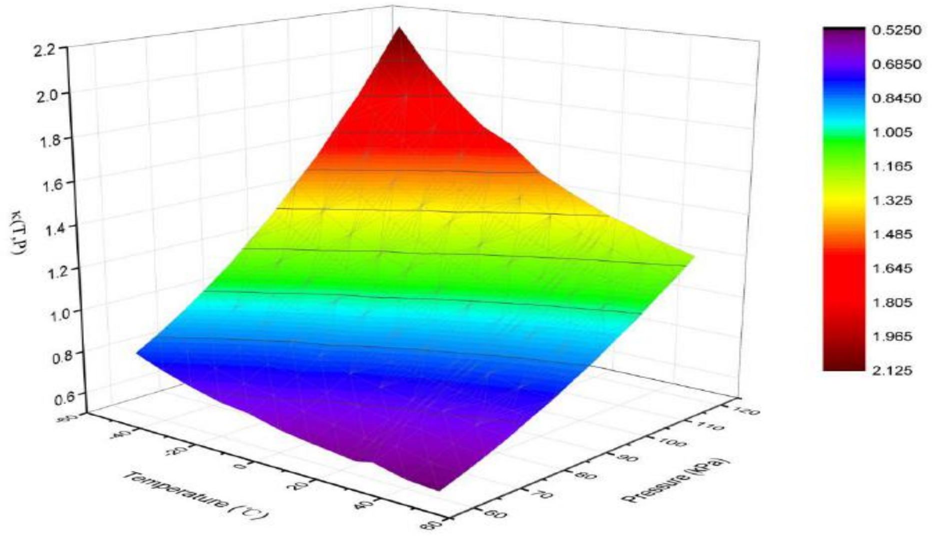
Flux calculation and WPL correction

$$q_c = q_{cm}\kappa \leftarrow \kappa = \bar{\kappa}\left(\bar{T},\bar{P}_e\right) + \left.\frac{\partial\kappa\left(\bar{T},\bar{P}_e\right)}{\partial T}\right|_{\bar{P}_e}\delta T + \left.\frac{\partial\kappa\left(\bar{T},\bar{P}_e\right)}{\partial P_e}\right|_{\bar{T}}\delta P_e + \ldots\Big\} \leftarrow P_e = P\left(1+\alpha_v x_v\right)$$

$$F_c = \mathbf{A}\left(\overline{w'q'_{cm}} + \mathbf{B}\mu\frac{\overline{q_{cm}}}{\overline{q_d}}\overline{w'q_v'} + \mathbf{C}(1+\mu\sigma)\frac{\overline{q_{cm}}}{\overline{T}}\overline{w'T'}\right)$$

where $\mathbf{A} = \bar{\kappa}$ $\quad \mathbf{B} = \left[1+\left(1-1.46\bar{x}_v\right)\alpha_v\bar{P}_e\frac{\kappa_{Pe}}{\bar{\kappa}}\right]$ $\quad \mathbf{C} = \left[1+\left(1-\bar{x}_v\right)\bar{T}\frac{\kappa_T}{\bar{\kappa}} + \bar{x}_v(\mathbf{B}-1)\right]$

3.48 for NH_3 and α_υ=2.48

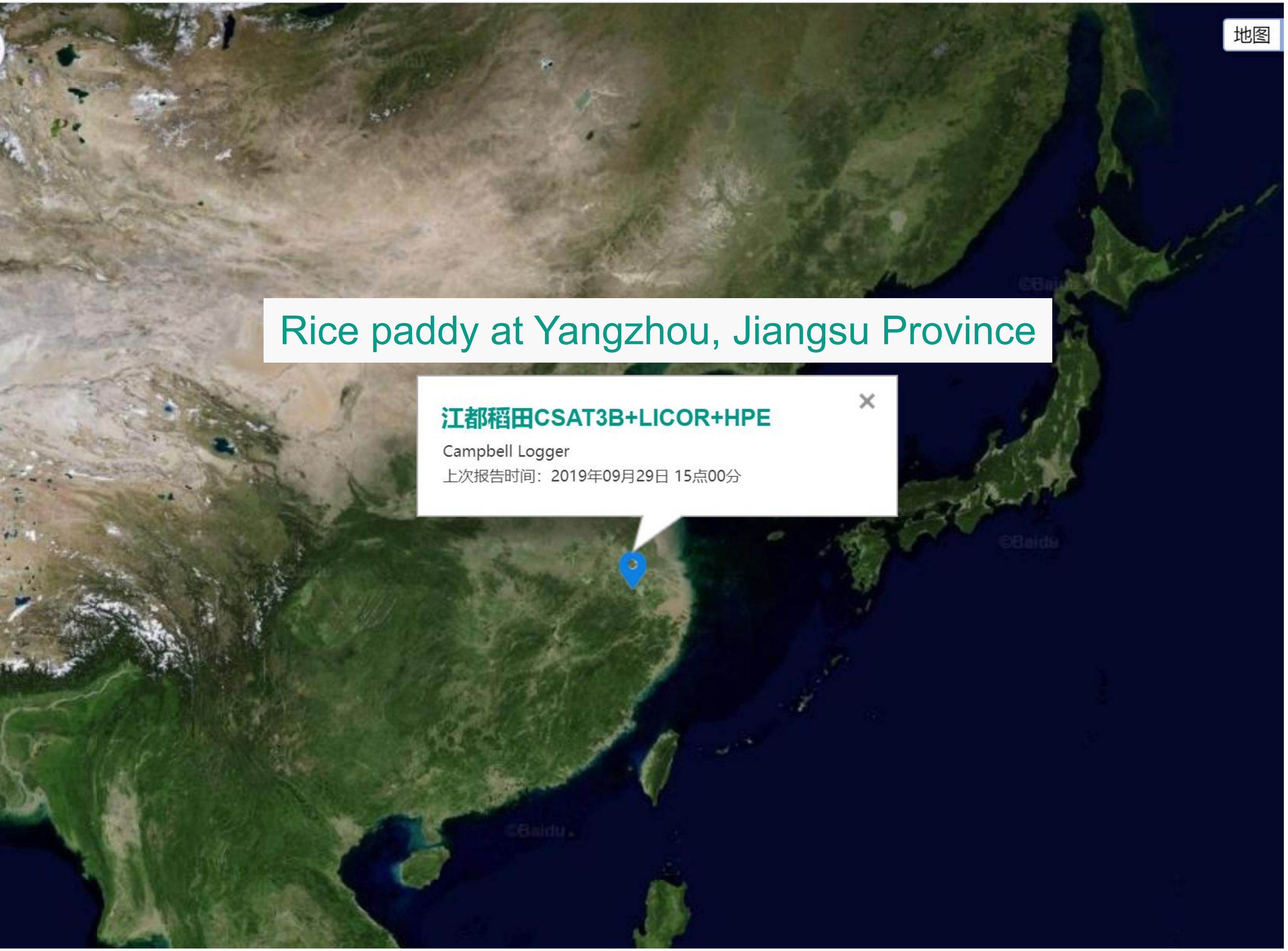


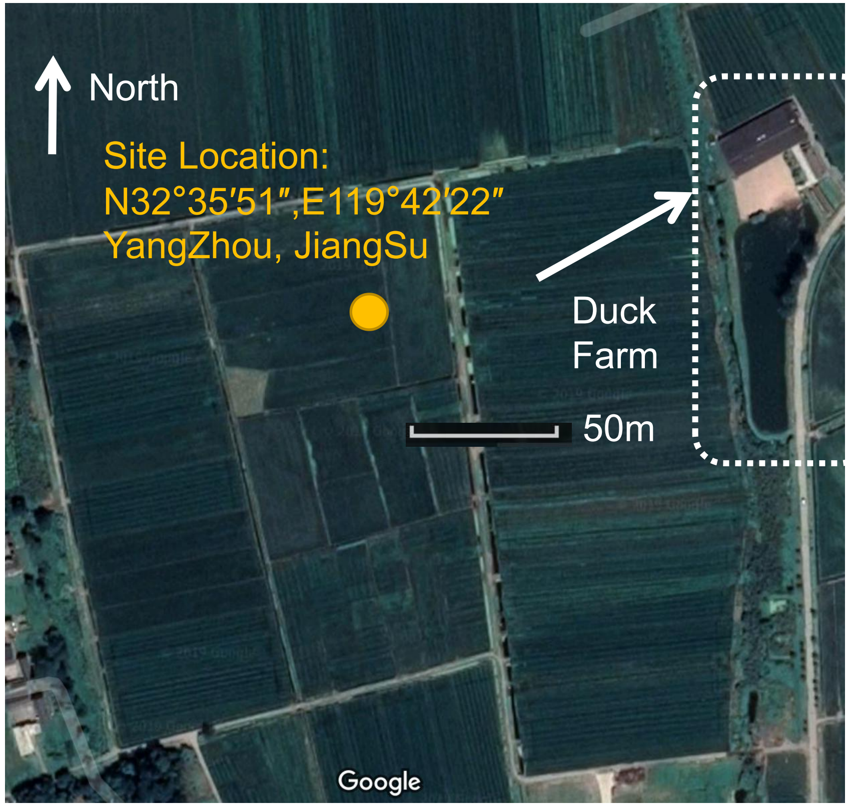
k(T,P) calculated for NH_3 lines @1102.3cm^{-1}

Addapted from:

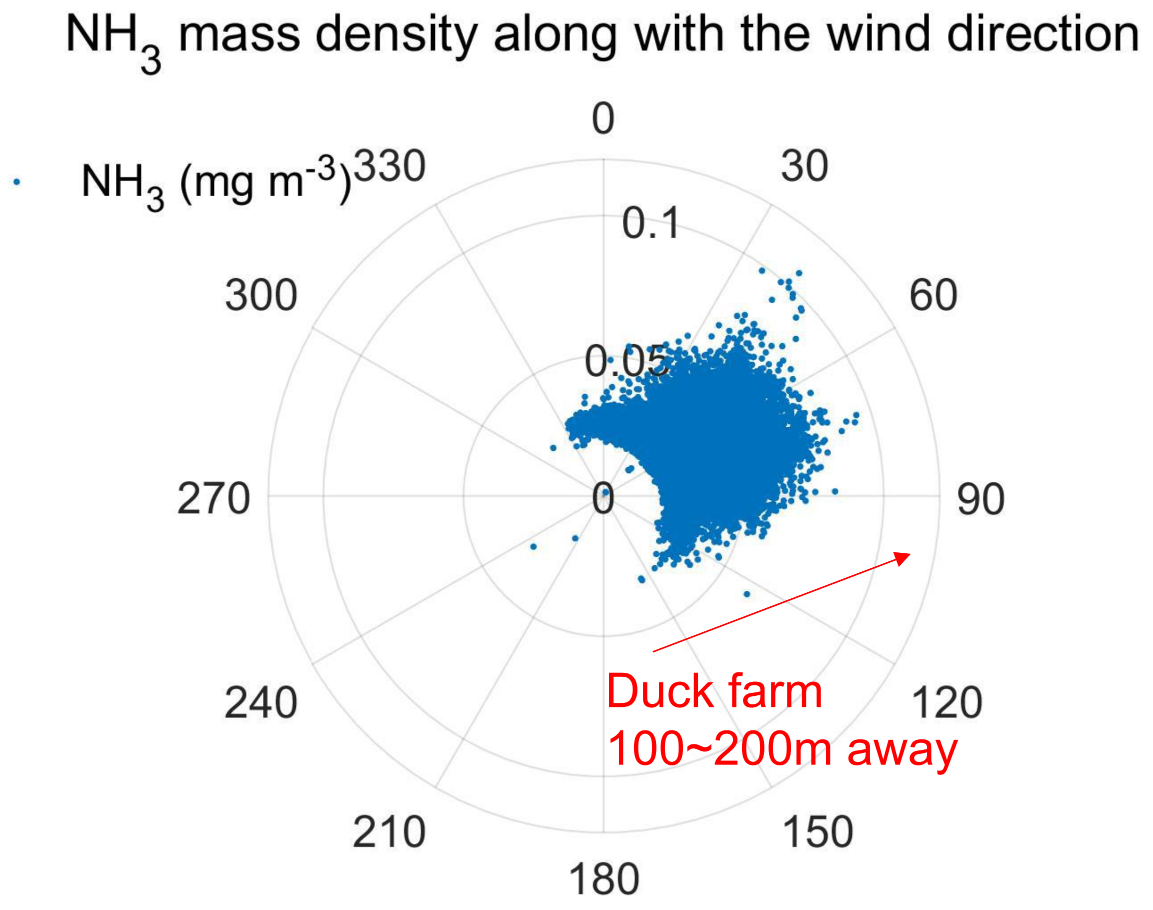
- G. Burba et. al., Accounting For Spectroscopic Effects in Eddy Covariance Measurements of Methane Flux. ***LICOR INC.***
- G. Burba et. al., Accounting for spectroscopic effects in laser-based open-path eddy covariance flux measurements. *Glob Change Biol*. 2019; 25:2189-2202. http://dio.org/10.1111/gcb.14614

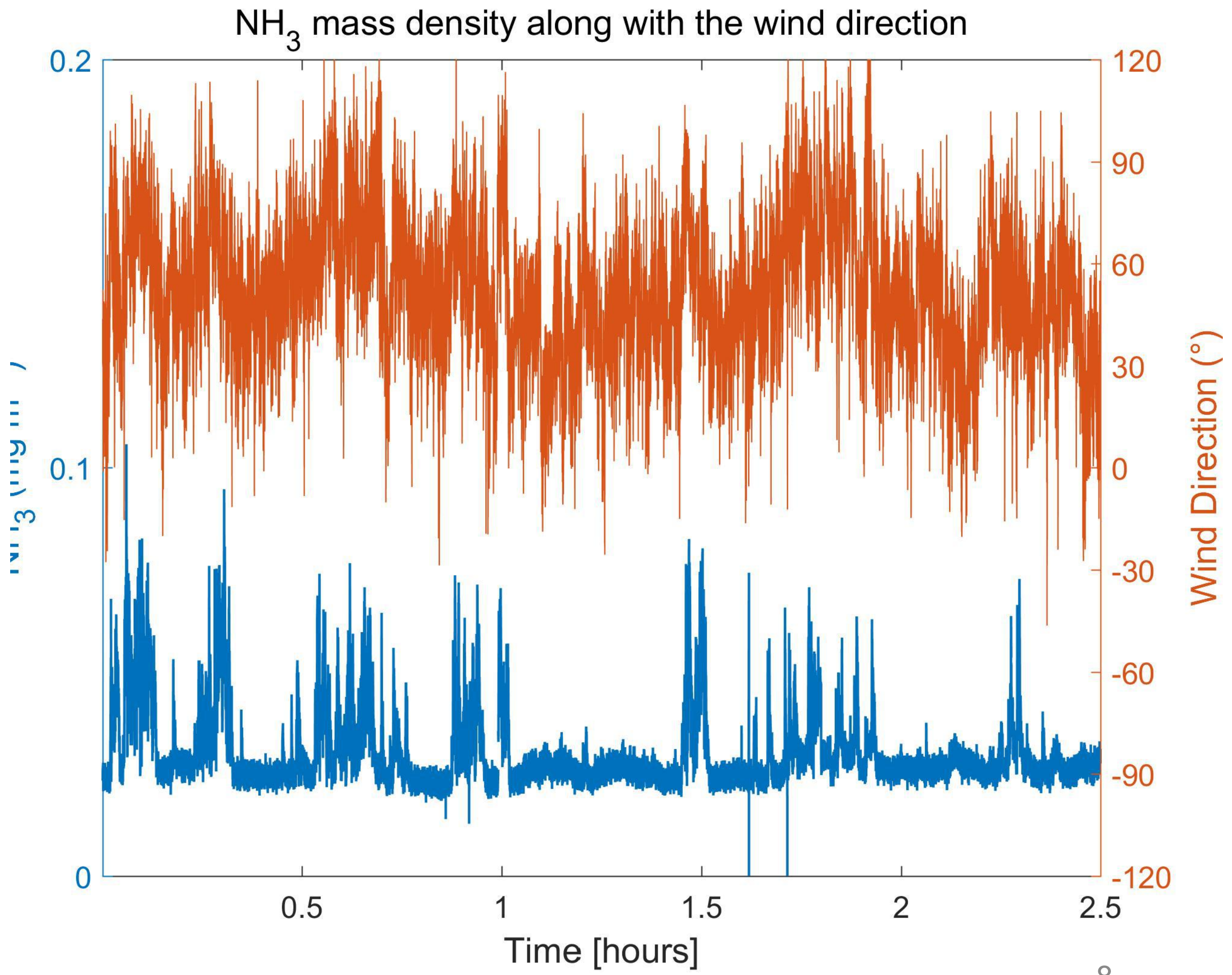
Field deployment 1: rice paddy (Sep. 2019)





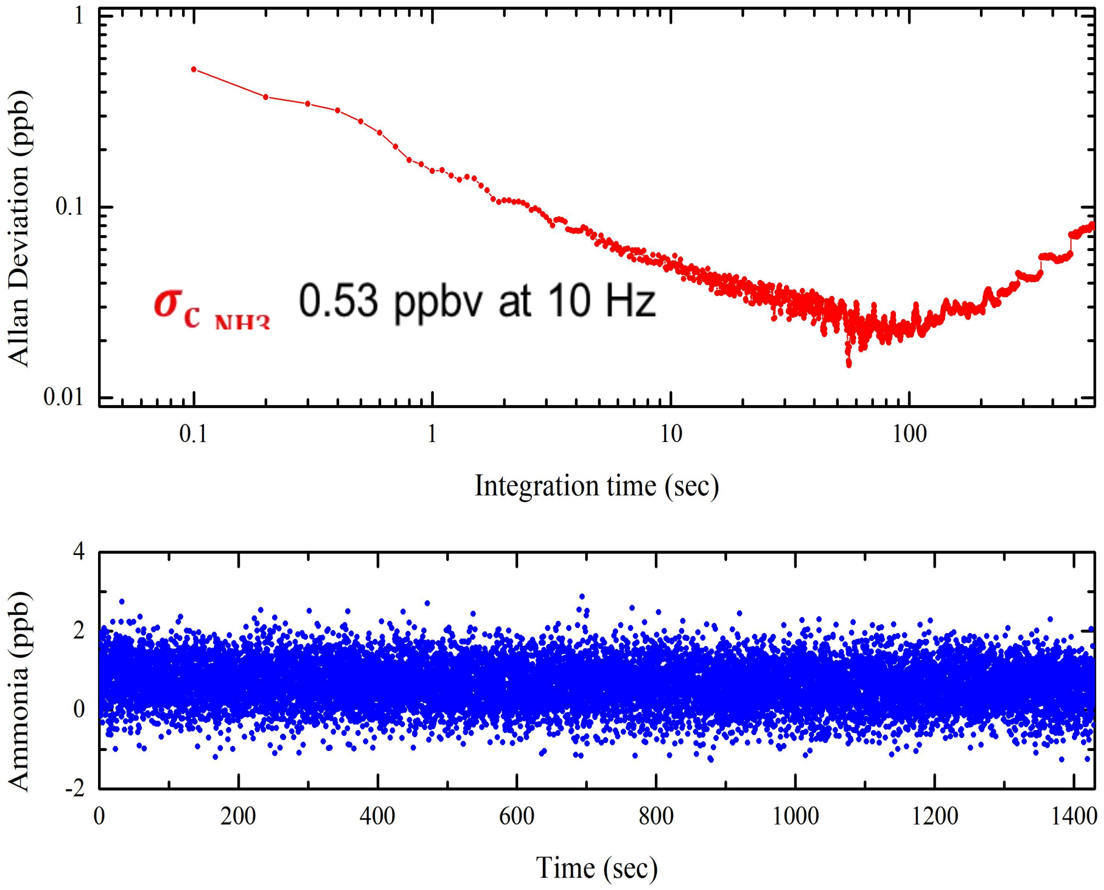
NH_3 mass density along with the wind direction



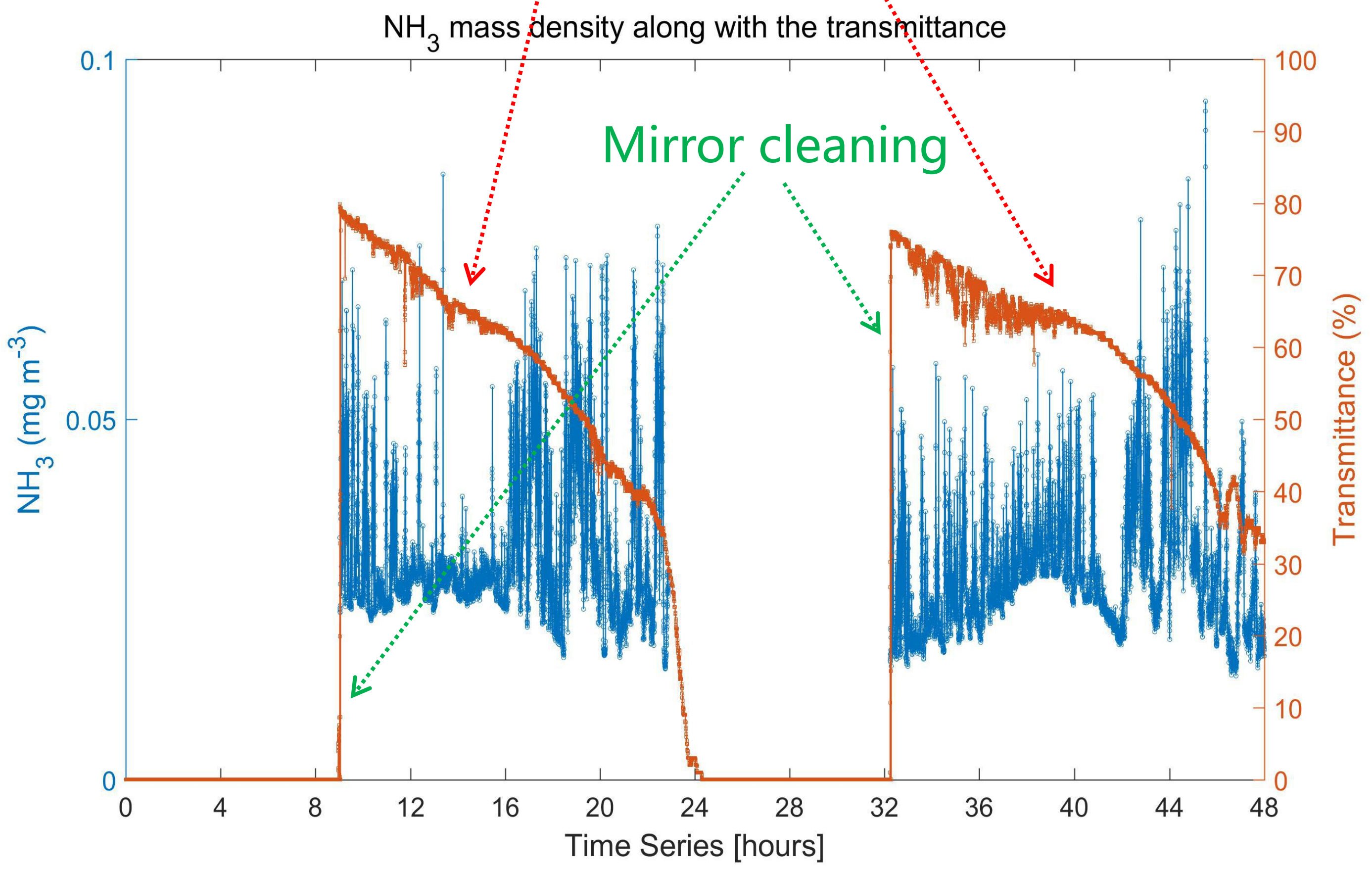


NH_3 analyzer performance and challenges

Optical signal reduction due to dust accumulate on mirrors

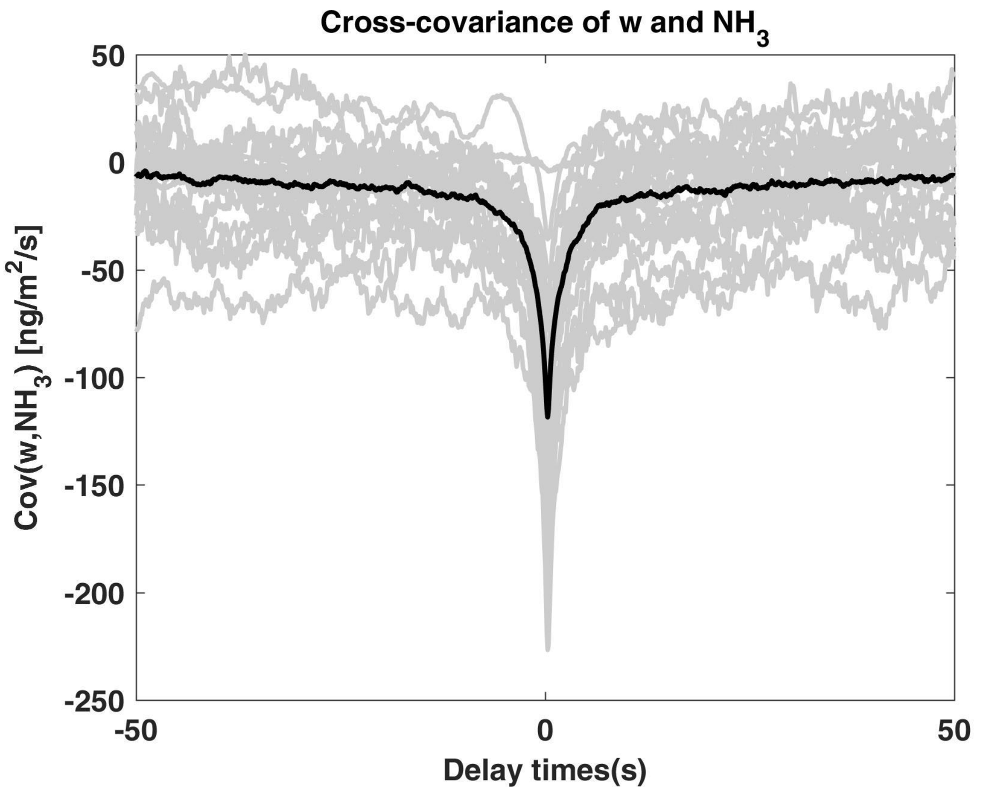


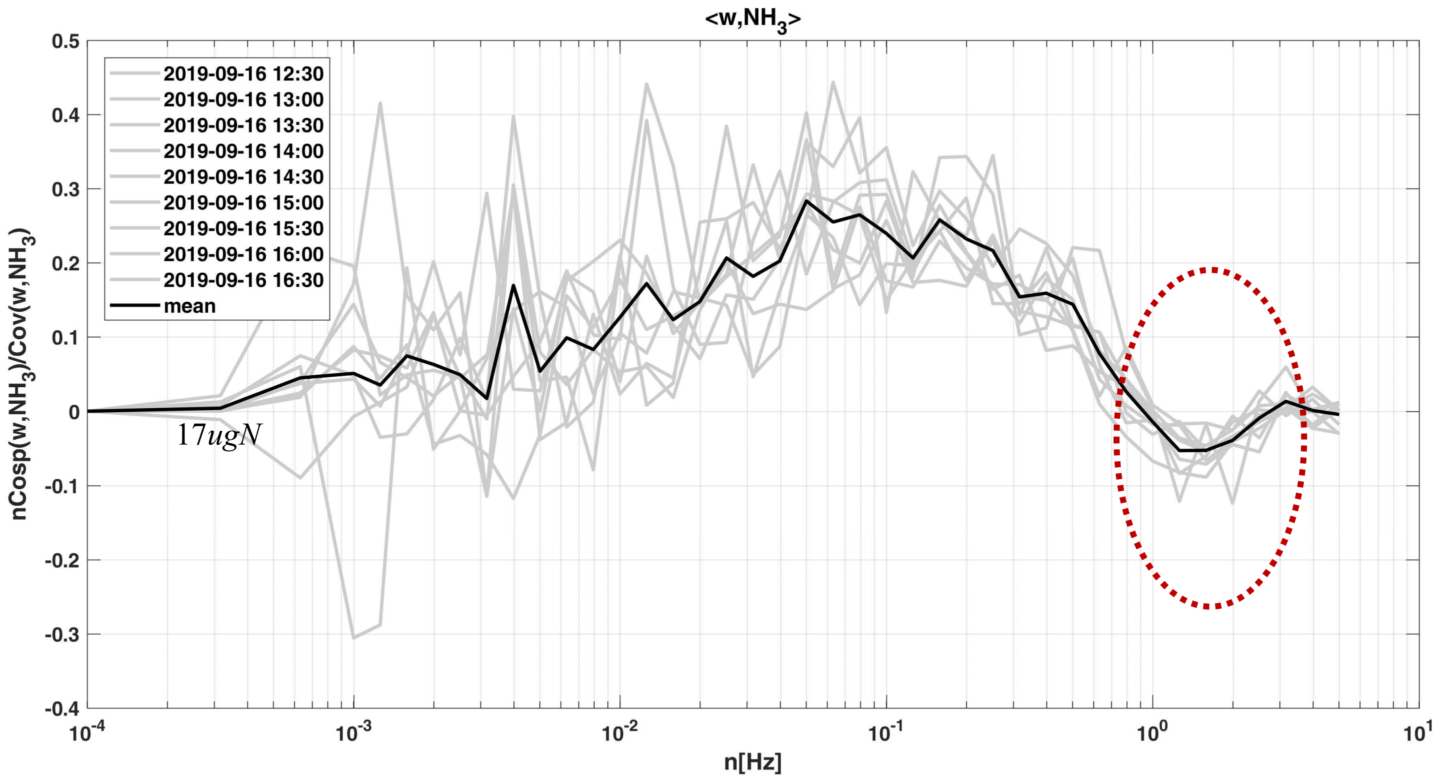
Allan Deviation analysis following Werle *et al*. (1993)



NH_3 concentration vs. Optical signal strength

NH_3 deposition due to duck farm close by





- Detection limit for half-hourly fluxes analysis following:

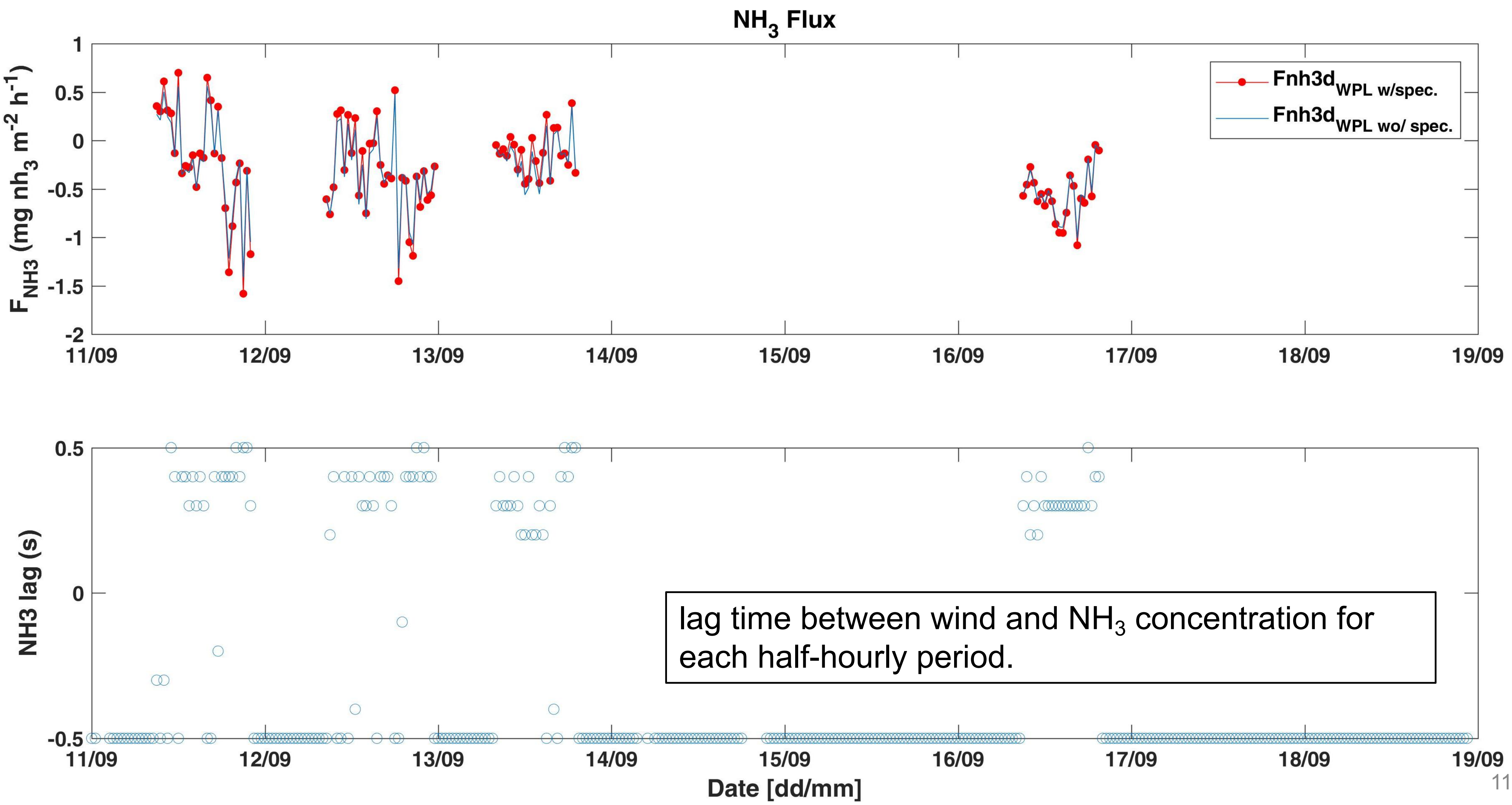
Wang K., et. al., (2020)

- The contribution of negative flux (deposition) mainly comes from high frequency

$$F_{det\_NH3} = \frac{2\sigma_w \times 2\sigma_{c\_NH3}}{\sqrt{fT}} \approx$$ 17 ug N m^{-2} h^{-1}

(95% confidence interval)

Continuous flux data



lag time between wind and NH_3 concentration for each half-hourly period.

Summary of field deployment 1

- **Achievements:**
  - A QCL based open-path analyzer has been deployed for the first time to measure atmospheric NH_3 with **~0.53 ppbv sensitivity at a 10Hz sampling rate.**
  - The standalone system (no PC required) consumes only **~ 50 Watts.**
  - An eddy covariance system equipped with this instrument showed a detection limit of ~**17 ug N m^{-2} h^{-1}** for half-hourly NH_3 fluxes from a rice paddy.
- **Challenges:**
  - High-frequency noise needs to be suppressed for higher flux detection sensitivity.
  - Automatic mirror cleaning at high dust area is needed to avoid signal attenuation.

Field deployment 2: dry rice paddy (Apr. 2020)

- Updated eddy covariance system: improving noise suppression for higher flux sensitivity

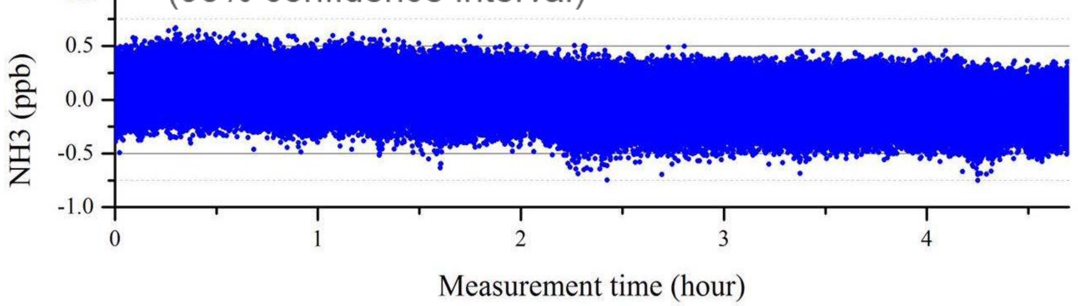
Upgraded system performance

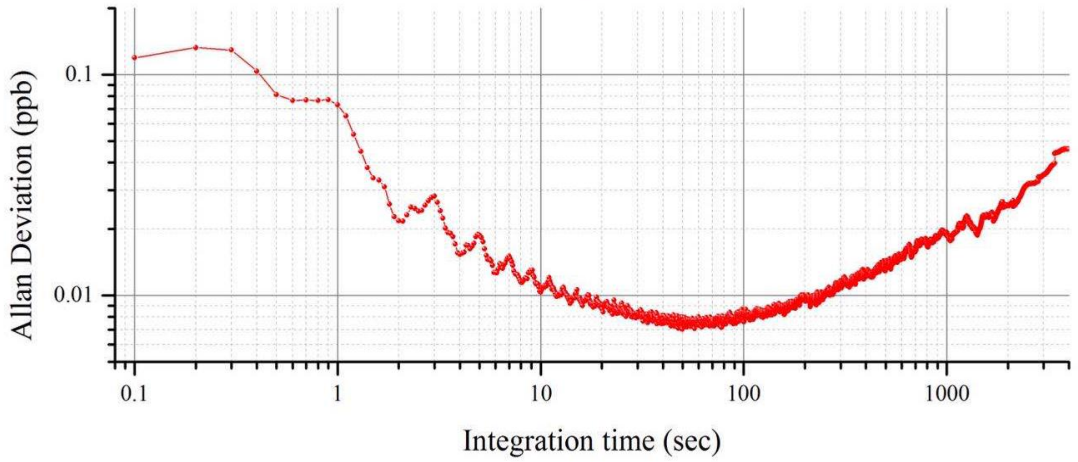
- NH_3 detection sensitivity was improved to **~0.11 ppbv at a 10Hz sampling rate.**
- The eddy covariance system showed an improved half-hourly flux detection limit of **~ 3.6 ug N m^{-2} h^{-1}**.

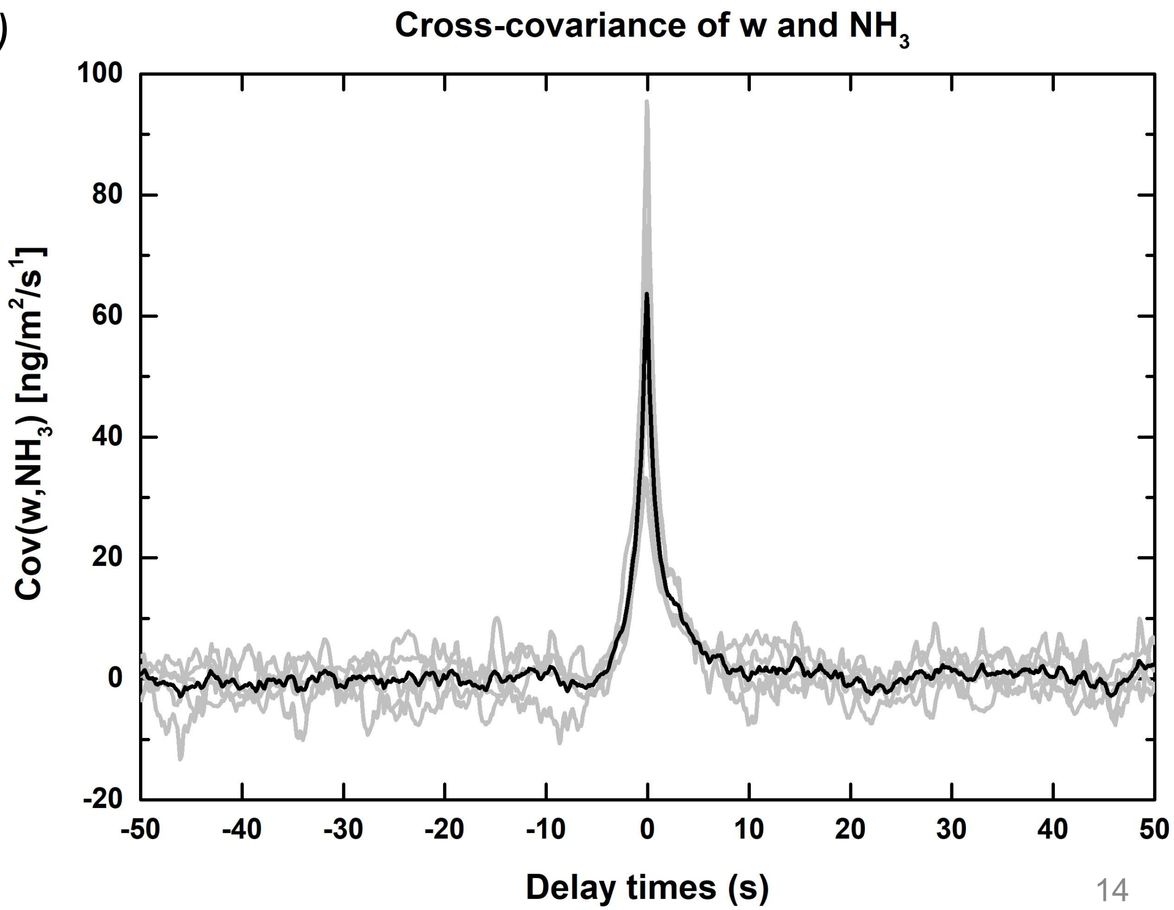
$$F_{det\_NH3} = \frac{2\sigma_w \times 2\sigma_{c\_NH3}}{\sqrt{fT}} \approx 1.0 \text{ ng N m}^{-2}\text{ s}^{-1}$$

(95% confidence interval)

Wang K., et. al., (2020)

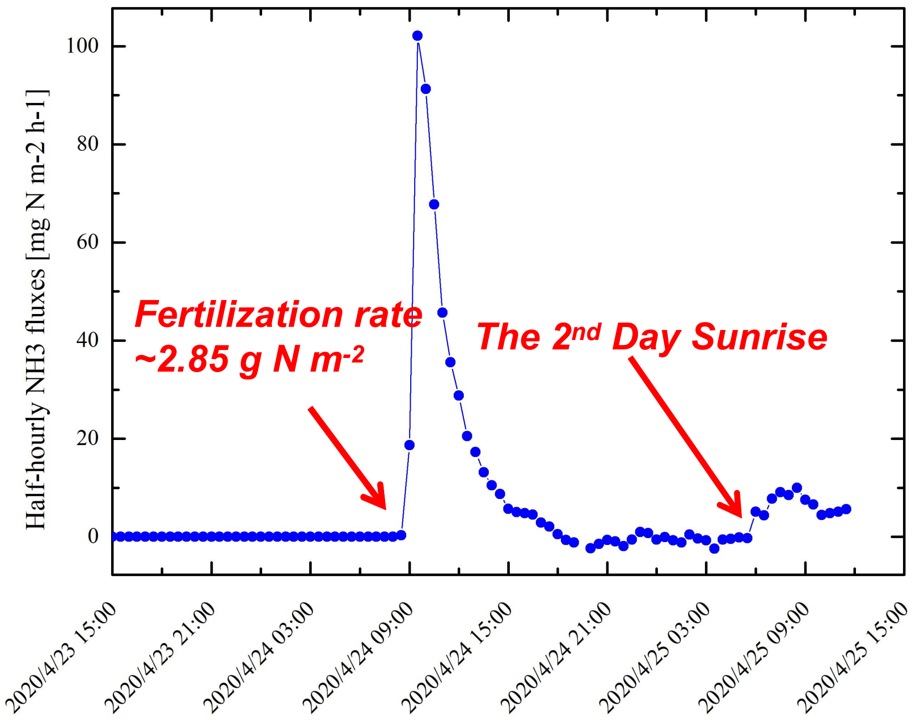




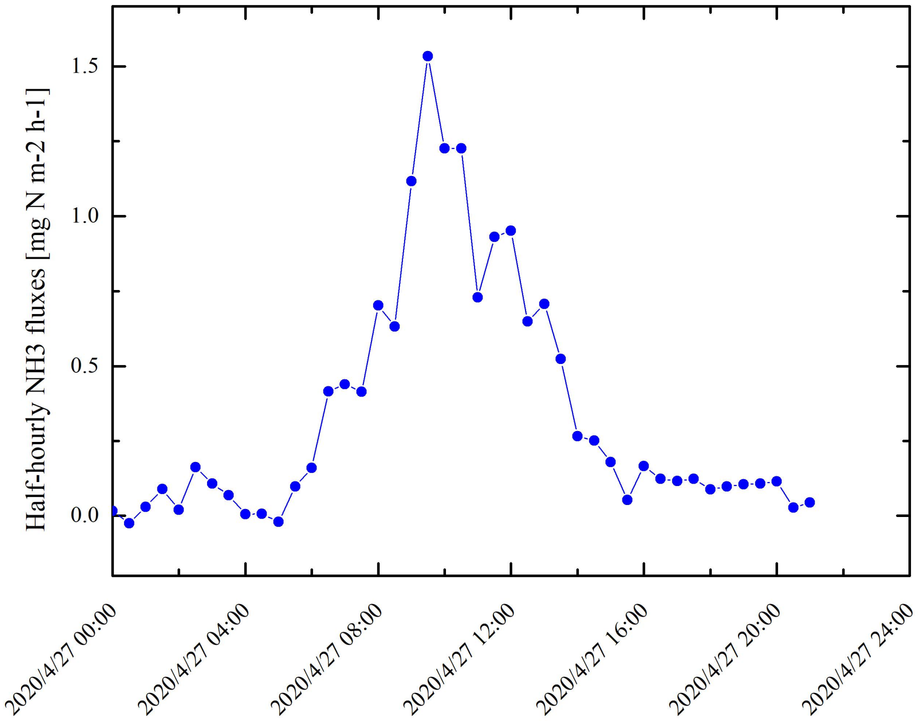


NH_3 fluxes before and after fertilizer application

An experiment with application of ammonium bicarbonate on a rice paddy during the fallow season

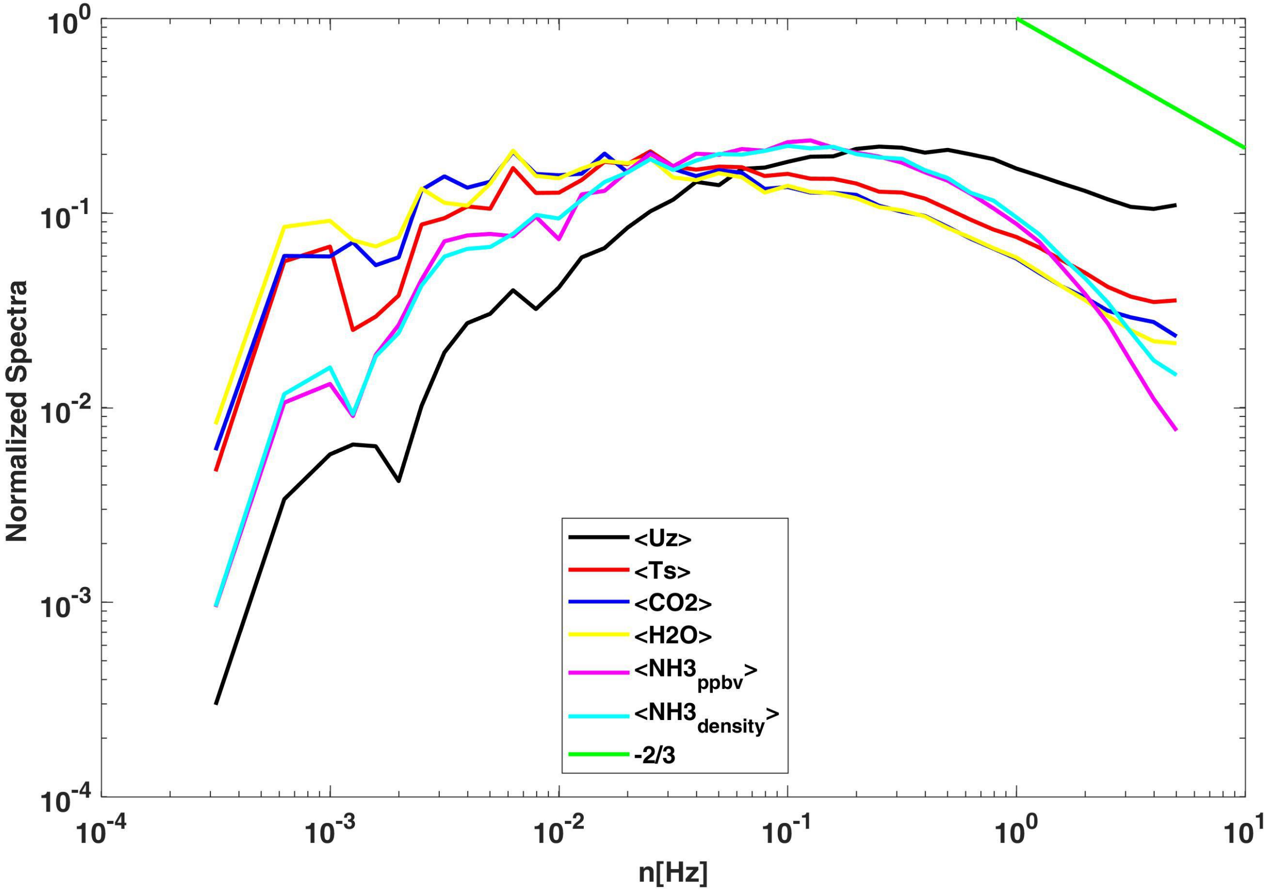


Half-hourly NH_3 fluxes before and after fertilizer application

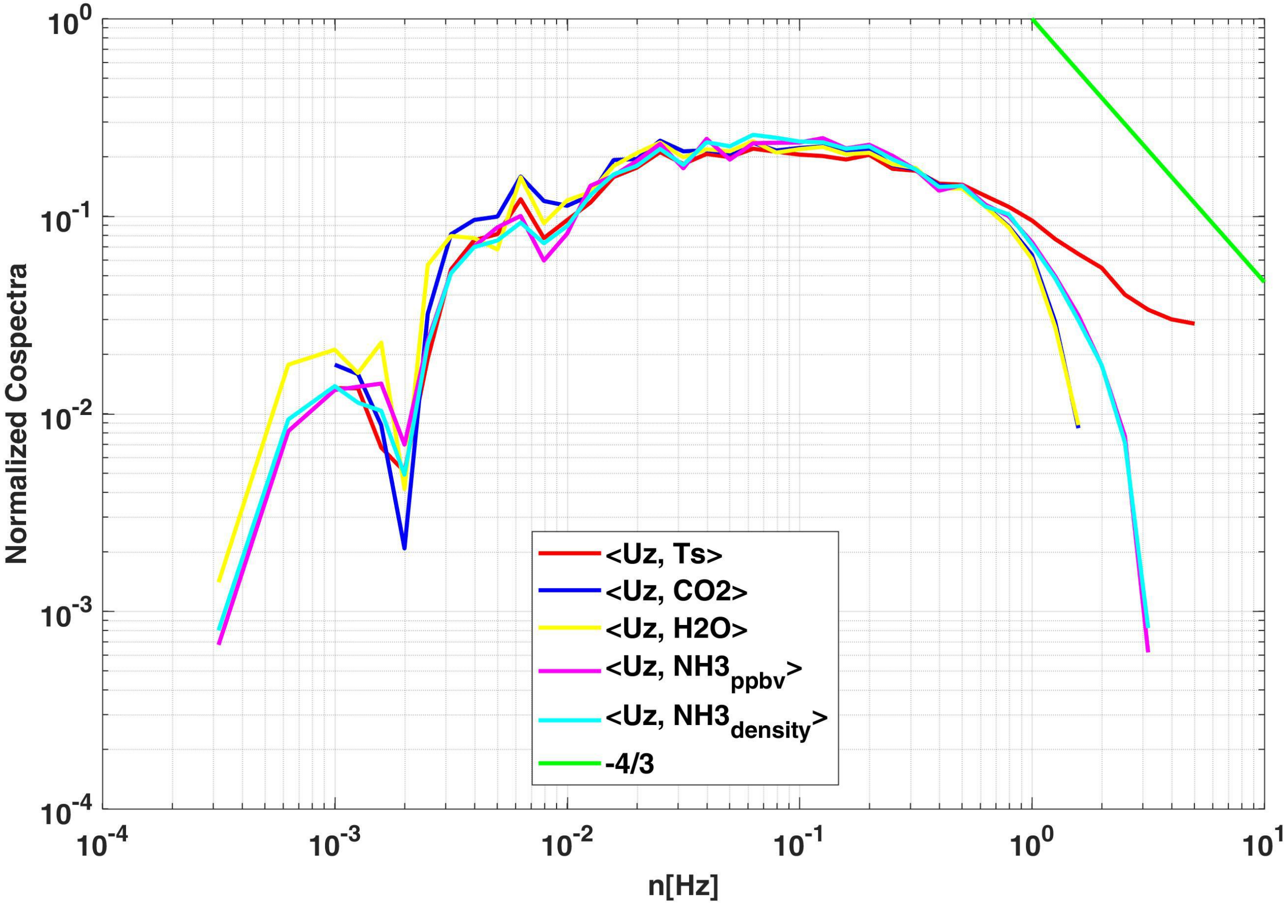


The 3rd day after fertilization, diurnal pattern can be observed clearly from night to midday

Spectra and Co-spectra



Spectra of w and Ts,CO_2,H_2O, NH_3



Co-spectra of w and Ts,CO_2,H_2O, NH_3

Conclusions & future works

Conclusion:

- An eddy covariance system equipped with an open-path QCL-based NH_3 analyzer (**model: HT8700, HealthyPhoton Co. Ltd.**, Ningbo, China) was deployed to measure the NH_3 fluxes from two subtropical rice paddies.
- The system showed a detection limit of **~ 3.6 ug N m^{-2} h^{-1}(95% confidence)**, for half-hourly fluxes, being capable of sensitively capture the NH_3 emission/deposition flux.
- NH_3 fluxes showed a diurnal pattern with local NH_3 emissions from morning to midday.

Future works:

- This eddy covariance system will be deployed and tested in virous types of ecosystem under different environmental conditions to ensure its long-term stability and reliability.
- We expect this system to be a powerful tool to measure the NH_3 emissions of all nitrogen fertilizer events, and the atmospheric NH_3 deposition in urban areas, and areas affected by agricultural and animal husbandry activities.

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- *TusStar*

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