An open-path QCL-based instrument with sub-ppbv sensitivity for eddy covariance measurement of NH$_3$ fluxes

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**NH₃ emissions in China**

- Ammonia (NH₃): a colorless gas with a pungent odor, very soluble in water, strong adsorption effect
  - a gas-phase precursor to PM2.5
  - form fine particle NH₄⁺ aerosols

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**NH₃ source contributions in China (2012)**

- **Livestock**: 52%
- **Fertilizer**: 29%
- **Biomass burning**: 4%
- **Agricultural soil**: 3%
- **Compost**: 3%
- **N-fixing crops**: 2%
- **Waste disposal**: 1%
- **Traffic**: 1%
- **Human excrement**: 1%
- **Chemical industry**: 0%
- **Ammonia escape**: 0%

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

Eddy covariance system

• NH₃ flux system: NH₃ 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

\[ q_c = q_{cm} \kappa \]

\[ \kappa = \kappa(T, P_c) + \frac{\partial \kappa(T, P_c)}{\partial T} \delta T + \frac{\partial \kappa(T, P_c)}{\partial P_c} \delta P_c + \ldots \]

\[ P_e = P(1 + \alpha_v x_v) \]

\[ F_e = A \left( w' q'_{cm} + B \frac{q_{cm}}{q_d} w' q_v + C \left( 1 + \mu \sigma \right) \frac{q_{cm}}{T} w' T' \right) \]

where

\[ A = \kappa \]

\[ B = \left[ 1 + \left( 1 - \frac{1}{\alpha_v} \right) \frac{\kappa(P_c)}{\kappa} \right] \]

\[ C = \left[ 1 + \left( 1 - x_v \right) \left( 1 - \frac{\kappa(P_c)}{\kappa} \right) + x_v \left( B - 1 \right) \right] \]

3.48 for NH\textsubscript{3} and \( \alpha_v = 2.48 \)

k(T,P) calculated for NH\textsubscript{3} lines @1102.3cm\textsuperscript{-1}

Addapted from:
• G. Burba et. al., Accounting For Spectroscopic Effects in Eddy Covariance Measurements of Methane Flux. LICOR INC.
Field deployment 1: rice paddy (Sep. 2019)

Rice paddy at Yangzhou, Jiangsu Province

Site Location:
N32°35'51'', E119°42'22''
YangZhou, JiangSu

Duck Farm
50m
NH\textsubscript{3} mass density along with the wind direction

- NH\textsubscript{3} (mg m\textsuperscript{-3})

Duck farm 100~200m away
NH₃ analyzer performance and challenges

Optical signal reduction due to dust accumulate on mirrors

Allan Deviation analysis following Werle et al. (1993)

NH₃ concentration vs. Optical signal strength
NH$_3$ deposition due to duck farm close by

- Detection limit for half-hourly fluxes analysis following:
  \[
  W. K., \text{et. al.}, (2020)
  \]

- The contribution of negative flux (deposition) mainly comes from high frequency
  \[
  F_{\text{det,NH}_3} = \frac{2\sigma_w \times 2\sigma_{\text{C,NH}_3}}{\sqrt{fT}} \approx 17 \text{ ug N m}^{-2} \text{ h}^{-1}
  \]
  (95% confidence interval)
Continuous flux data

![Graph showing NH₃ Flux with data points for F_{NH₃} and lag time between wind and NH₃ 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 $\text{~0.53 ppbv sensitivity at a 10Hz sampling rate.}$
  • The standalone system (no PC required) consumes only $\text{~50 Watts.}$
  • An eddy covariance system equipped with this instrument showed a detection limit of $\text{~17 ug N m}^{-2} \text{h}^{-1}$ 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

rice field at Ningbo, Zhejiang Province
Upgraded system performance

- NH\textsubscript{3} detection sensitivity was improved to $\sim 0.11$ ppbv at a 10Hz sampling rate.
- The eddy covariance system showed an improved half-hourly flux detection limit of $\sim 3.6$ ug N m\textsuperscript{-2} h\textsuperscript{-1}.

$$F_{\text{det,NH}_3} = \frac{2\sigma_w \times 2\sigma_{C,NH_3}}{\sqrt{fT}} \approx 1.0 \text{ ng N m}^{-2} \text{ s}^{-1}$$

Wang K., et. al., (2020)
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 3$^{rd}$ day after fertilization, diurnal pattern can be observed clearly from night to midday
Spectra and Co-spectra

Spectra of $w$ and $T_s$, $CO_2$, $H_2O$, $NH_3$

Co-spectra of $w$ and $T_s$, $CO_2$, $H_2O$, $NH_3$
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 $\sim 3.6$ 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 various 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.
Acknowledgement

- State Key Laboratory of Atmospheric Boundary Layer Physics and Atmospheric Chemistry, Institute of Atmospheric Physics, Chinese Academy of Sciences, Beijing, China
- Jiangsu Tynoo Corporation, Wuxi, Jiangsu
- Joe, Zhou
- Ningbo Innovation Fund
- TusStar

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