Measuring ammonia losses from pastures with micrometeorological methods

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Motivation

- NH₃ emission is an important part of the N budget of agricultural ecosystems
- Grazing is assumed to be a mitigation option for NH₃ emission from livestock.
- But representative NH₃ emission measurements from pastures are rare.
- For grazed pastures, a high spatial (and temporal) variability has to be expected, which is difficult to cover by chambers/windtunnels

- micrometeorological methods for pasture NH₃ exchange
  - integration over medium/large source area (footprint): c. 0.1 – 1 ha
  - no alteration of ambient conditions (temperature, humidity, …)
  - no sorption on chamber walls
Measurement challenges for ammonia fluxes

published inter-comparison experiments:

von Bobutzki et al. (2010)

Milford et al. (2009)

desired instrumental capabilities:

• reliable and stable concentration measurement
• fast time response → for EC application (despite ‘stickiness’ of NH$_3$)
• able to resolve large concentration and flux ranges
Gradient Measurement Systems

- Mean concentrations on two heights (synchronous if possible)

‘Lift’-gradient-systems
- moving tube inlet
- (old) Picarro
cavity-ringdown analyser

GRAEGOR system
- 2 AMANDA denuders
- IC-detection

2 AiRRmonia analysers
- Membrane scrubbers
- Conductivity detectors
- Cross switching of detectors

[Wolff et al., 2010, AMT]

[Flechard et al., 2010, BG; Spirig et al., 2010, BG]
Backward Lagrangian stochastic (bLS) modelling

- Use of horizontal concentration gradient/difference
- Requires a spatially limited source area
- Measurements of
  - mean concentrations upwind and downwind of the source
  - turbulence characteristics (u, u*, z/L)
- Applied analyzers:
  - impingers (Sintermann et al., 2011)
  - miniDOAS (based on Volten et al., 2012)
- Use of WindTrax model (cf. Wilson et al., 2013)
- Validation with artificial NH₃ source (tube grid with orifices)
MiniDOAS line sensors for bLS application

- UV absorption spectroscopy (200 – 230 nm)
- UV-lamp → retro-reflector → spectrometer
- Open path-length typically 20…60 m (x2)
- Optimisation of design for mobile use
Comparison of bLS methods with miniDOAS and impingers
Eddy Covariance (EC) method

- Eddy covariance (EC) is a method to measure trace gas exchange…
  - on the field scale (integration over areas in the order of 0.2-1.0 ha)
  - without alteration of the ambient conditions
  - in a physically direct way (without major ideal assumptions)
  - consistently with state-of-the-art GHG flux measurements

- Eddy covariance requires a continuous fast response concentration measurement (< 1 sec.) at one single position

\[ F_c = w(t) \cdot c(t) \]

- \( w \) : vertical wind speed
- \( c \) : trace gas concentration
EC system with HT-CIMS analyser (based on PTR-MS)

- EC setup with strong heating of drift tube & inlet line
- captured very large concentration fluctuations
- fast time response (1-2 s) with inlet line in the field

[Sintermann et al., 2011, AMT]
EC system with QCL and inertial inlet

- quantum cascade laser (QCL-TILDAS-76, Aerodyne Res.)
- Short inlet tube (4 m)
- Glass inlet and tube heating (40 °C) to avoid wall adsorption
- An ‘inertial inlet’ box at the inlet removes particles (possible reactants for NH$_3$)

A sharp turn of the sample flow after the critical orifice removes particles (>300 nm)

[Ellis et al., 2010; Ferrara et al., 2012]
EC system with QCL: time response

- cross covariance function (with distinct flux peak)
- High-frequency damping quantification by ‘ogive method’ (in comparison to sensible heat flux) → c. 30% flux loss

\[ v'NH3_{ppb}(\tau): |MAX| = -0.019 \quad @ \quad \tau = -0.2s, \quad \sigma = -0.018 \]

\[ \text{ogive } v'NH3_{ppb} \quad @ \quad \tau = -0.2s \]
EC system with QCL: results

- semi-natural peatland site surrounded by intensive livestock production (~1 km distance)
- Continuous deposition fluxes with variability closely linked to concentration
Fast response NH$_3$ detection by conversion to NO

- **NO** chemiluminescence detector (CLD) [e.g. Rummel et al., 2002]

- Detection of other N$_r$ compounds using suitable fast response converters:
  - NO$_2$ $\rightarrow$ NO by photolytic converter [e.g. Stella et al., 2013]
  - NO$_y$ $\rightarrow$ NO by thermal catalytic converter
    [e.g. Munger et al., 1996; Horii et al., 2006; Geddes and Murphy, 2014]
  - $\sum$N$_r$ $\rightarrow$ NO by thermal conversion (steel at 800°C) + gold converter
    [Marx et al., 2012; Ammann et al., 2012; Brümmer et al., 2013]

- This study: combination of parallel NO$_y$ and $\sum$N$_r$ converter for mast mounting

NH$_3$ (or NH$_x$) is measured as the difference of the 2 channels ($\sum$N$_r$ – NO$_y$)
EC system with converter: field setup

- Measurements on mast in the center of the pasture field
- Converters must be placed at the sample air inlet (close to the sonic anemometer) to avoid wall sorption and reactions in the tube
Comparison of $\sum N_r$ converter channel to individual compound measurements

- NO, NO$_2$: CLD TEI 42C + BLC
- NH$_3$: Picarro CRDS
Comparison of NO$_y$ converter channel to individual compound measurements

- NO, NO$_2$: CLD TEI 42C + BLC

![Graph showing NO, NO$_2$, and NO$_y$ concentrations over time.]
Validation of NH$_3$ concentration measurements

$$\text{NH}_3 = \sum N_r - \text{NO}_y$$
Flux quality Issues

- A high-frequency damping loss of 15-35% was found depending on stability and windspeed → correction based on ogive analysis

- Non-stationarity of the ambient $N_r$ concentration represents the main limitation for flux measurements in this agricultural/polluted area and necessitates a careful QA/QC processing (still improving) → use of running average (24h or 3h) for display
Pasture Site

- Swiss Central plateau, near Posieux
- 3.7 ha pasture field with rotational grazing in 6 paddocks
- 20 dairy cows (milking in barn 2x day\(^{-1}\))
- EC flux tower ▲
- Main wind directions: NE & SW
- Fertiliser application: c. 80 kgN ha\(^{-1}\) year\(^{-1}\) (1x slurry + 1x mineral)

12:00 – 16:00
Effect of fertiliser application on NH$_3$ emission

- Very low temperature during slurry application

![Graph showing NH$_3$ flux, air temperature, and NO$_y$ flux for slurry and urea applications with markers for specific dates and temperature values.](image-url)
‘Background’ NH$_3$ flux (grazing season)

- 25 days after last fertiliser application
- in comparison with NO$_y$ exchange
Exchange of NH\textsubscript{3} (background/grazing)

- Mostly (net) NH\textsubscript{3} emissions, highest in spring and lowest in autumn/winter
- Measured NO\textsubscript{y} flux includes NO emission

- Seasonal mean diurnal cycles be used for simple upscaling to entire year (separation of fertilizer events and grazing/‘background’)

![NH\textsubscript{3} flux graphs for spring, summer, and autumn](image-url)
Conclusions

- The combination of the 2-channel NO analyser (EcoPhysics CLD 899) with the 2-channel thermal converter allows the measurement of concentration and EC fluxes of NH$_3$ (or rather NH$_x$).

- A moderate high-frequency flux damping has to quantified and corrected for: 20-35% for low measurement heights (2 m)

- NH$_3$ (and NO$_y$, NO$_2$, NO) eddy covariance fluxes have been measured over a grazed pasture

- The investigated pasture mostly showed NH$_3$ emission depending on temperature, fertiliser application, and grazing activity (fresh excreta)

- EC fluxes provide spatially integrated net fluxes with high time resolution and relatively high precision
  → problem of partitioning between parallel NH$_3$ emission and deposition
Work in Progress / Outlook

EC-Converter system design/setup and data processing:

- optimization of flow regime (lower response time): e.g. orifice arrangement → reduced flux damping damping
- synchronization of both channels to reduce noise effect in NOy for NH3 measurements
- quantify influence of red noise (non-stationarity on flux detection → optimization of filtering procedure

Field applications:

- Presently ongoing inter-comparison of EC-QCL, EC-Converter, and bLS-miniDOAS systems over pasture
- Next year (planned): comparison of micrometeorological methods with chamber/windtunnel measurement to investigate the source contribution of dung and urine patches
Thank you for your attention

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Comparison of bLS and IHF methods

Cumulated emission (kg N ha$^{-1}$)

23.09.2014 00:00  23.09.2014 12:00  24.09.2014 00:00  24.09.2014 12:00

DOAS + bLS
Impinger + bLS
Impinger IHF
Conversion efficiency tests

The preparation (mixing) or analysis of calibration gas mixtures for specific components is often problematic and may have a considerable uncertainty.

[Marx et al., 2011]
\[ \sum N_r \text{ converter principle} \]

Combination of oxidizing and reducing converter

**TRANC** – a novel fast-response converter to measure total reactive atmospheric nitrogen

O. Marx\(^1\), C. Brümmer\(^2\), C. Ammann\(^3\), V. Wolff\(^3\), and A. Freibauer\(^2\)
Fast response of NH$_3$ detection

- response of NO detector CLD899

- \( \Sigma N_f \) channel after slurry application (20 cts \( \approx \) 1 ppb)
Effect of fertiliser application on NH$_3$ and N$_2$O emission

- application rates (mineral/TAN): 30-50 kgN ha$^{-1}$
Summary of reactive N gas exchange (year 2013)

- Simple upscaling of mean diurnal cycles to seasonal emissions
- Similar importance of fertilizer application events and background emissions for NH₃ (in contrast to NO and N₂O)
- Strong seasonality for NO and NH₃ emission, but not for N₂O emissions
Motivation I: Nitrogen budget and gaseous emissions of pasture with grazing animals

- Surface volatilisation: $\text{NH}_3$
- Fertilizer: $(N_{\text{min}}, N_{\text{org}})$
- Nit./denitrification: $(\text{NO}, \text{N}_2\text{O}, \text{N}_2)$
- Leaching: $(\text{NO}_3^-)$
- Biological fixation: $(\text{N}_2)$
- Dry deposition: $(\text{NH}_3, \text{NO}_y)$
- Wet deposition: $(\text{NH}_4^+, \text{NO}_3^-)$
- Animal weight gain, milk: $(N_{\text{org}})$
Concentrations and EC fluxes of NO and NO$_2$
Measurement method: Eddy Covariance (EC)

- flux footprint: effective source area of measured trace gas flux