Measuring ammonia losses from pastures with micrometeorological methods

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- ❖ Eddy Covariance systems using fast response analyzers
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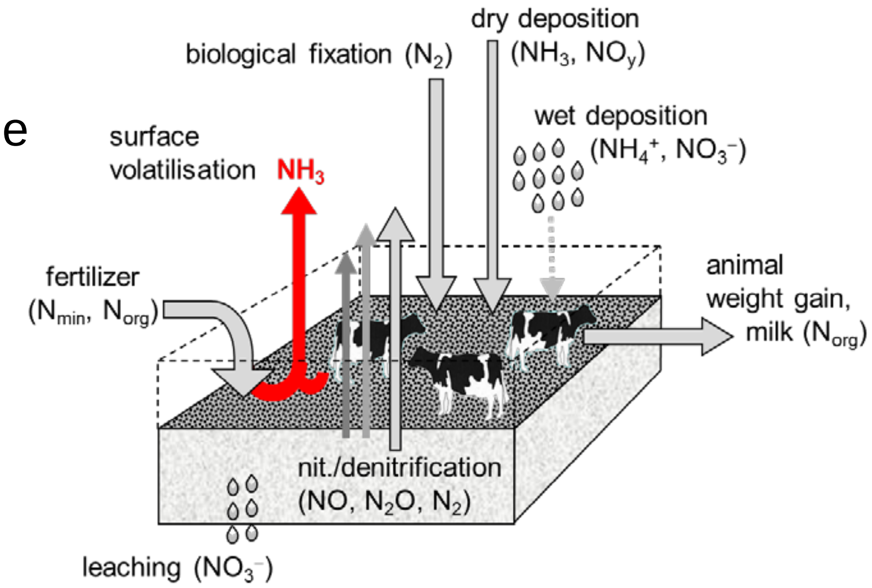
Motivation



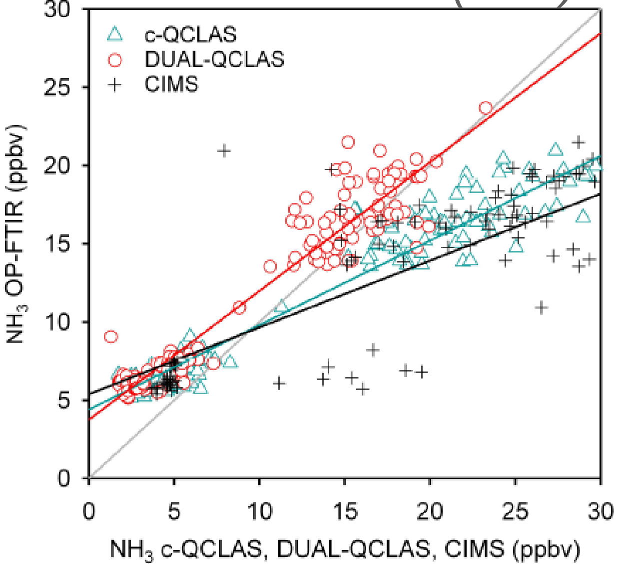
- NH_3 emission is an important part of the N budget of agricultural ecosystems
- Grazing is assumed to be a mitigation option for NH_3 emission from livestock.
- But representative NH_3 emission measurements from pastures are rare.
- For grazed pastures, a high spatial (and temporal) variability has to be expected, which is difficult to cover by chambers/windtunnels

➢ micrometeorological methods for pasture NH_3 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

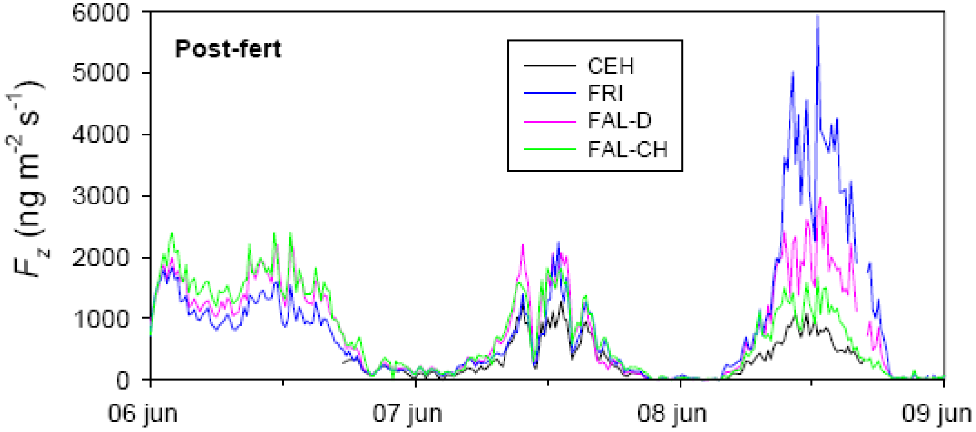
Measurement challenges for ammonia fluxes

published inter-comparison experiments:

von Bobrutzki 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

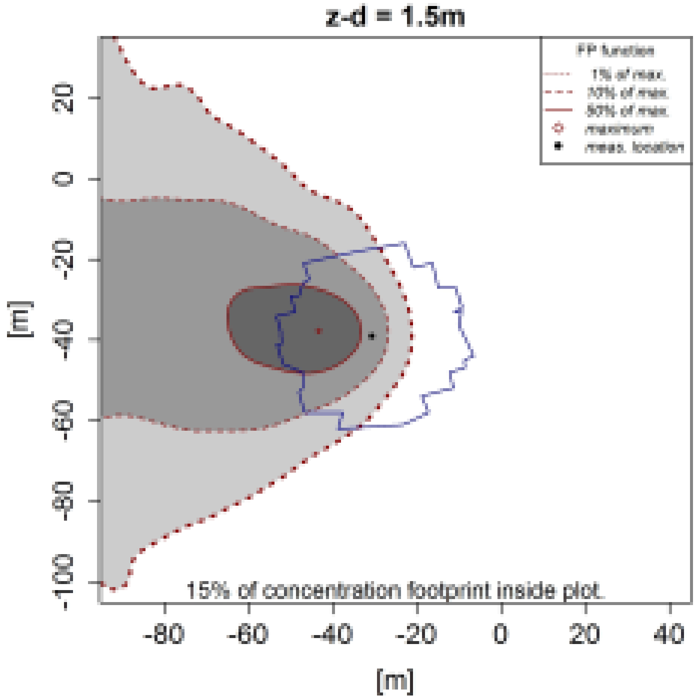
[Wolff et al., 2010, AMT]

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

[Flechard et al., 2010, BG;
Spirig et al., 2010, BG]

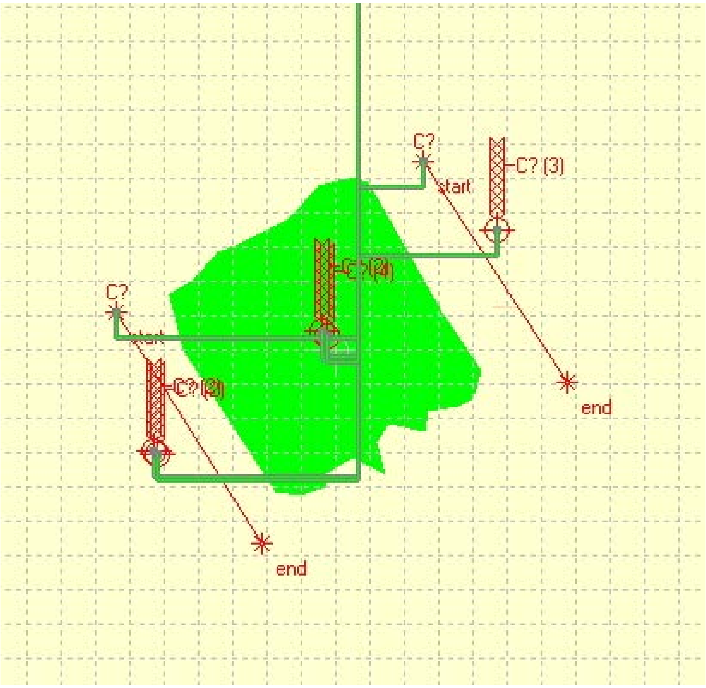
Backward Lagrangian stochastic (bLS) modelling

- 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 NH_3 source (tube grid with orifices)

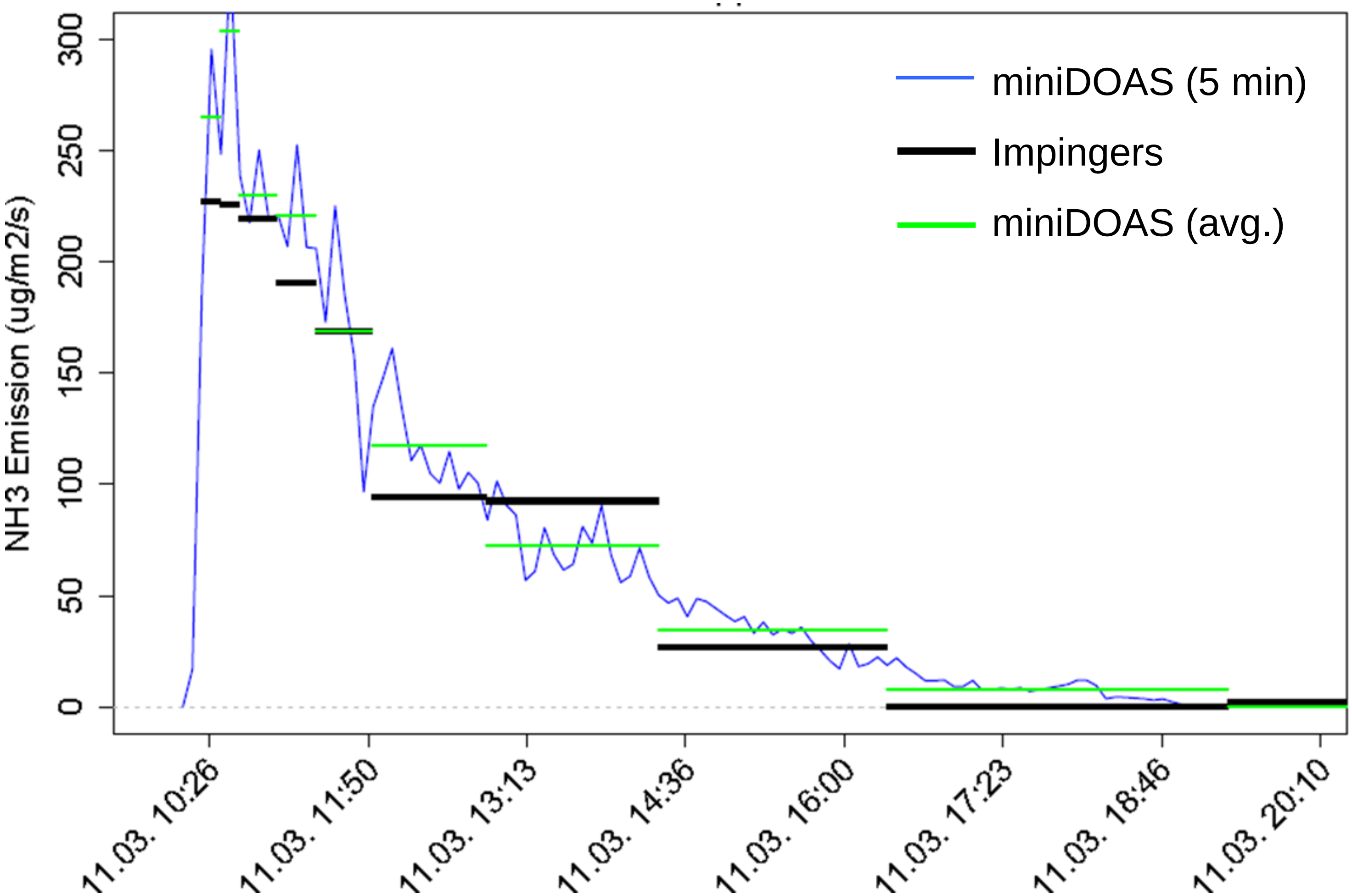


MiniDOAS line sensors for bLS application

- ❖ 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

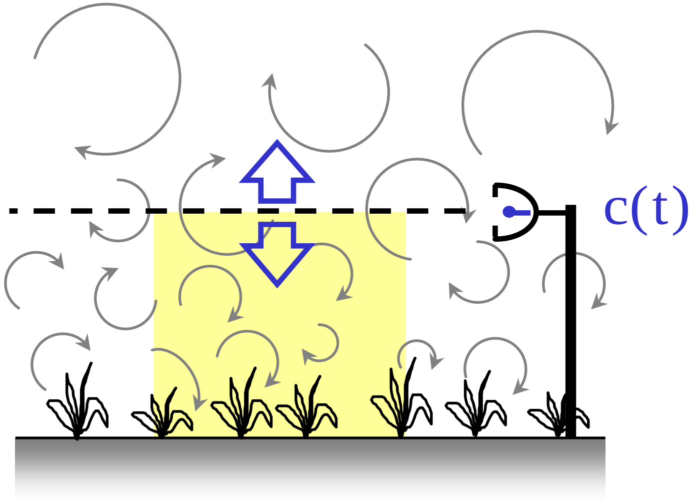


Comparison of bLS methods with miniDOAS and impingers



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



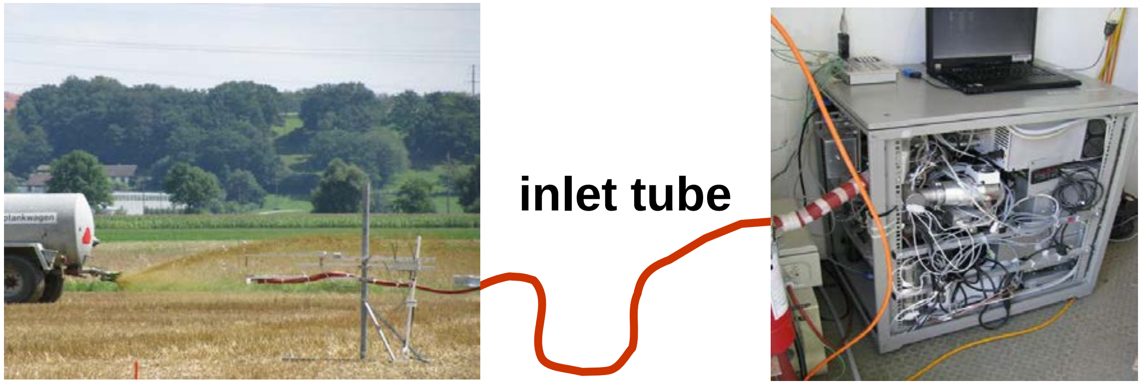
w : vertical wind speed

c : trace gas concentration

$$\boxed{F_c = \overline{w(t) \cdot c(t)}}$$

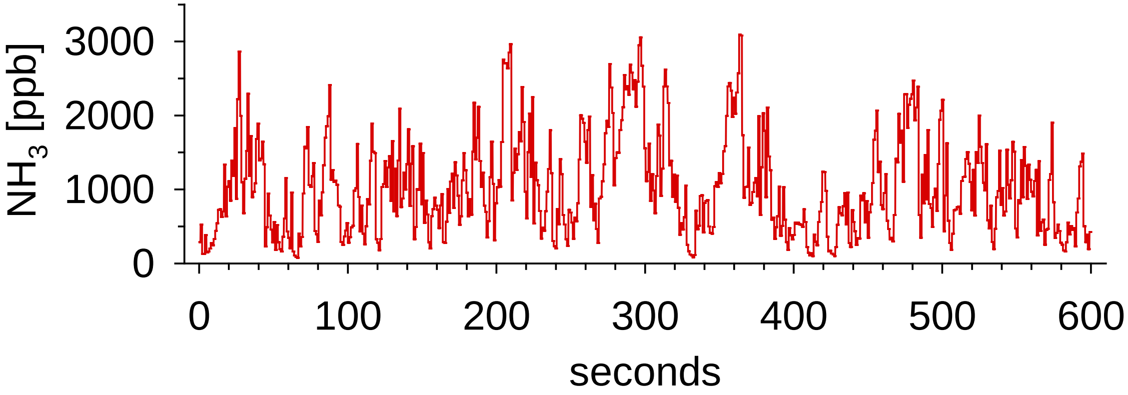
EC system with HT-CIMS analyser (based on PTR-MS)

- EC setup with strong heating of drift tube & inlet line



23 m, ½“, PFA, 100 l min^{-1}, heated to 150°C

- captured very large concentration fluctuations
- fast time response (1-2 s) with inlet line in the field



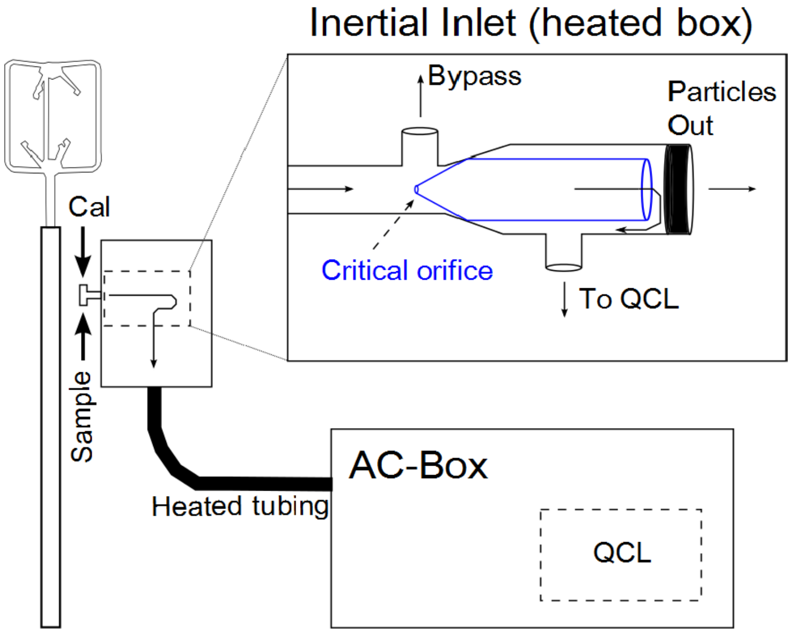
[Sintermann et al., 2011, AMT]

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)

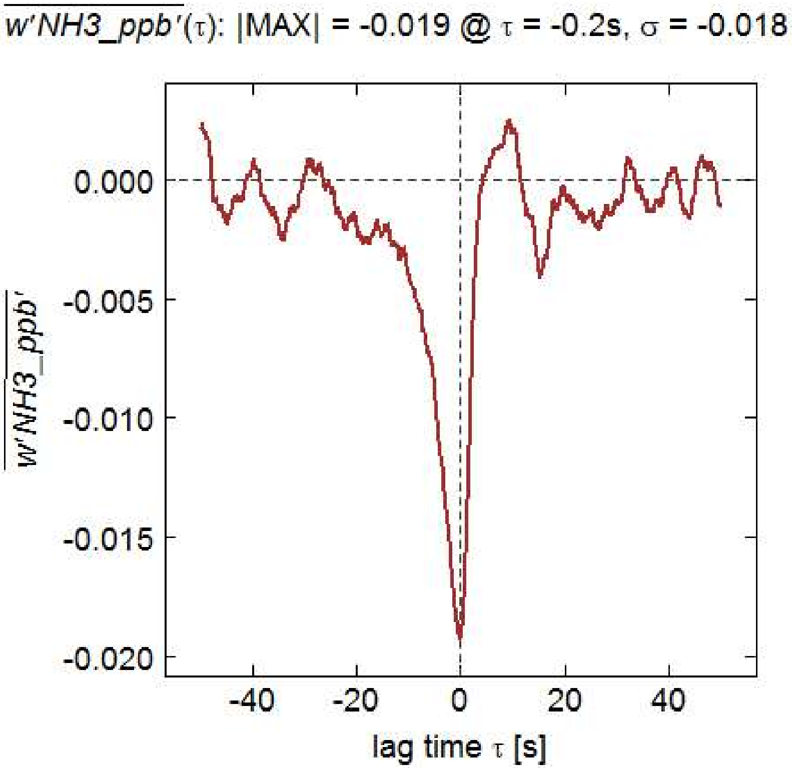
A sharp turn of the sample flow after the critical orifice removes particles (>300 nm)

[Ellis et al., 2010; Ferrara et al., 2012]

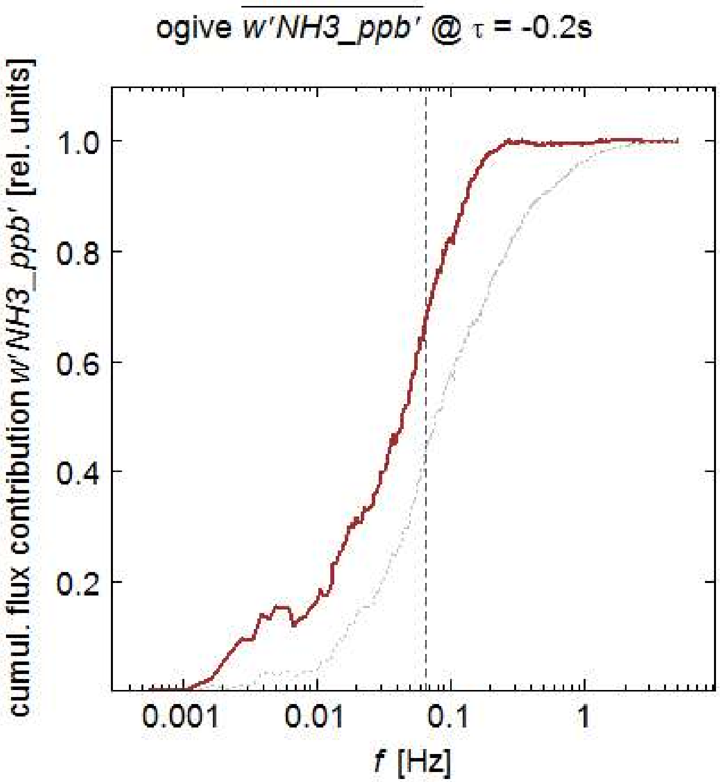


EC system with QCL: time response

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



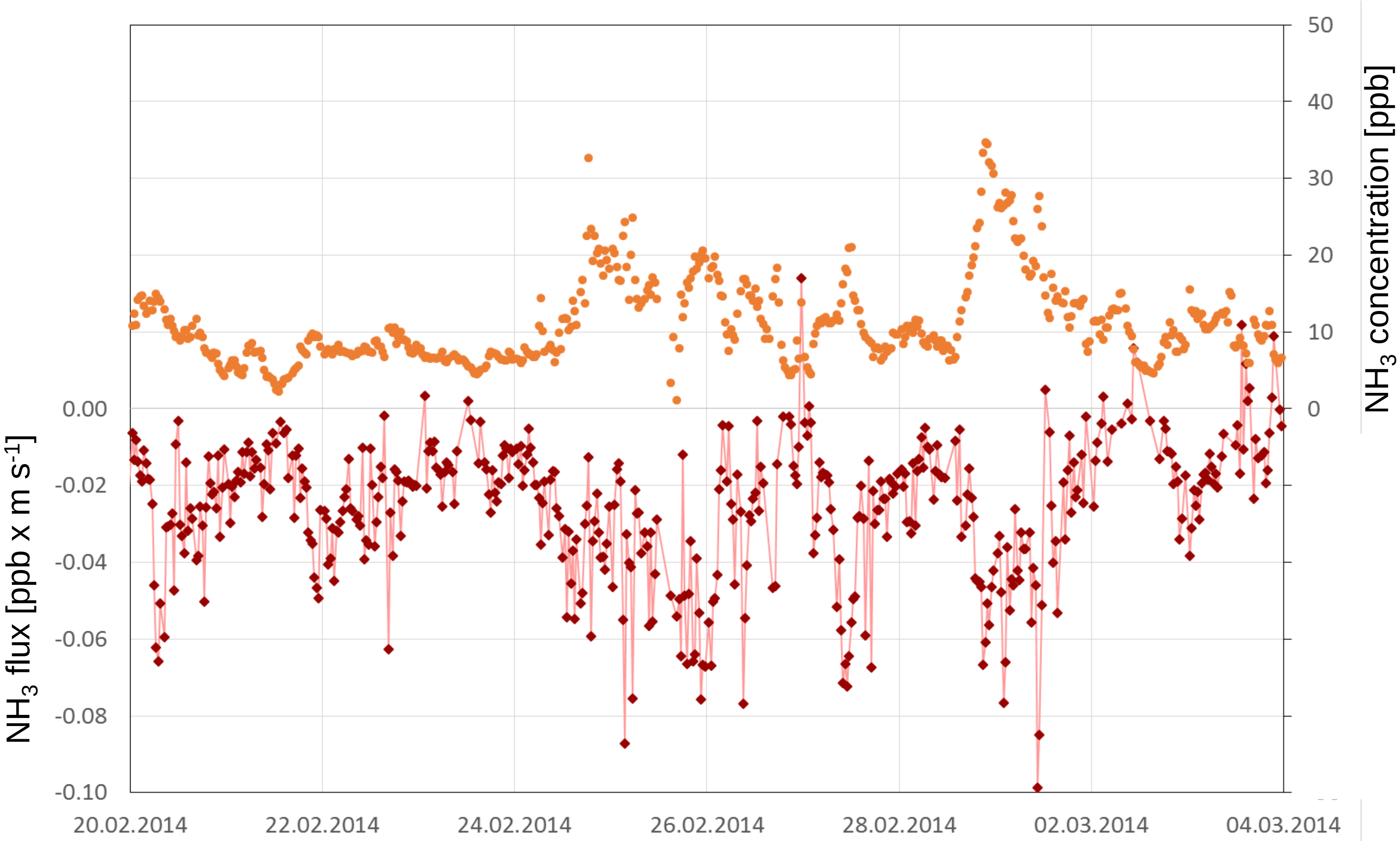
$\overline{w'NH3\_ppb'}(\tau)$: |MAX| = -0.019 @ τ = -0.2s, σ = -0.018



ogive $\overline{w'NH3\_ppb'}$ @ τ = -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

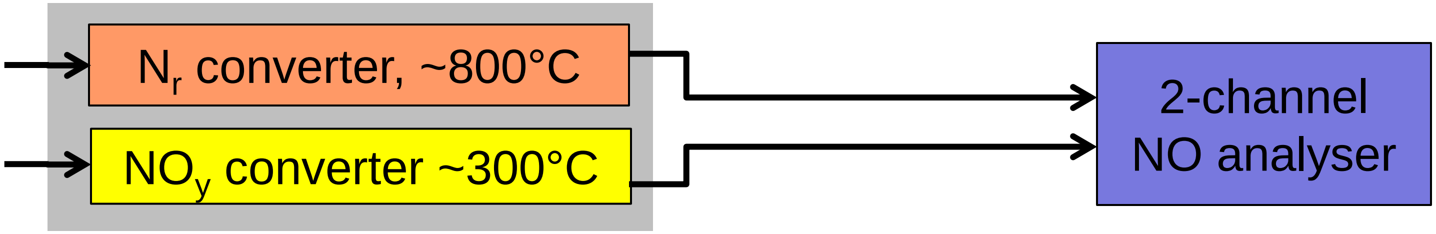
- NO chemiluminescence detector (CLD) [e.g. Rummel et al., 2002]
- Detection of other N_r compounds using suitable fast response converters:

NO_2 → NO by photolytic converter [e.g. Stella et al., 2013]

NO_y → NO by thermal catalytic converter
[e.g. Munger et al., 1996; Horii et al., 2006; Geddes and Murphy, 2014]

$\sum N_r$ → NO by thermal conversion (steel at 800°C) + gold converter
[Marx et al., 2012; Ammann et al., 2012; Brümmer et al., 2013]

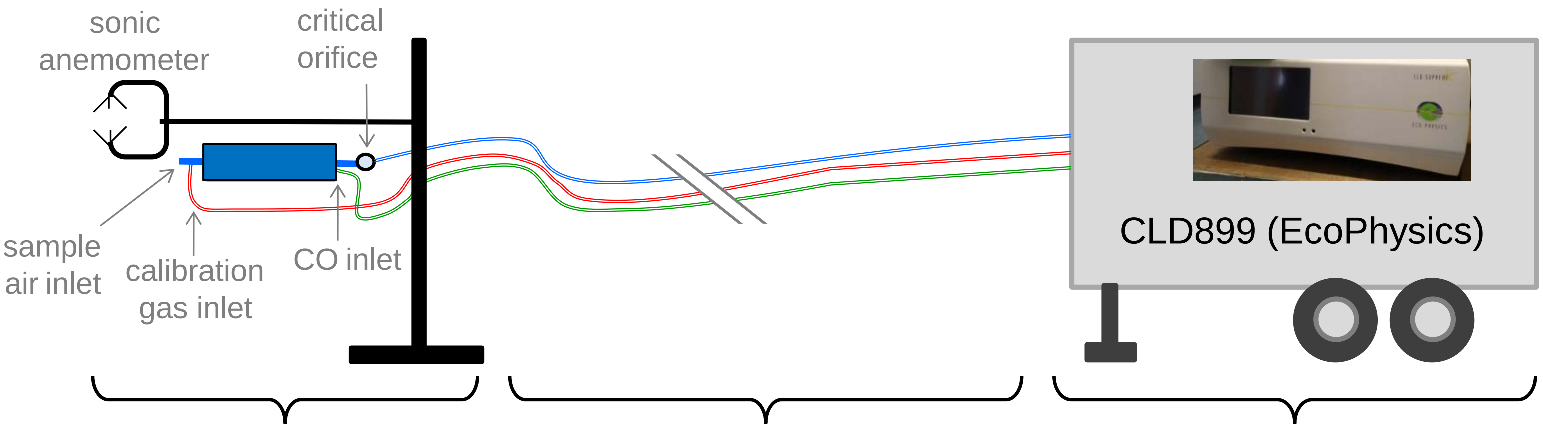
- This study: combination of parallel NO_y and $\sum N_r$ converter for mast mounting



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

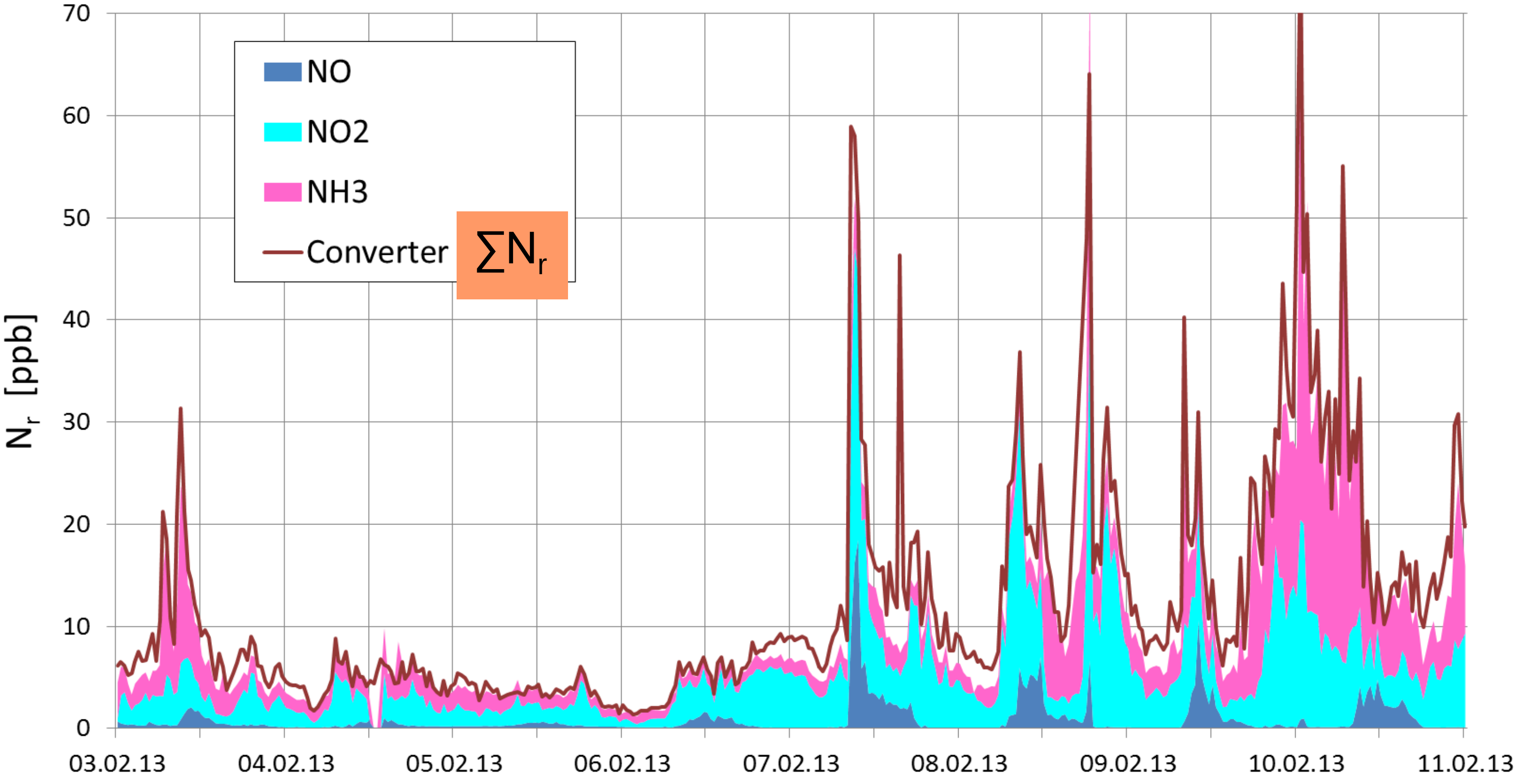


sample, calibration, and CO tubing with 20 m length

trailer housing for CLD analyser, data acquisition, cal. gases etc.

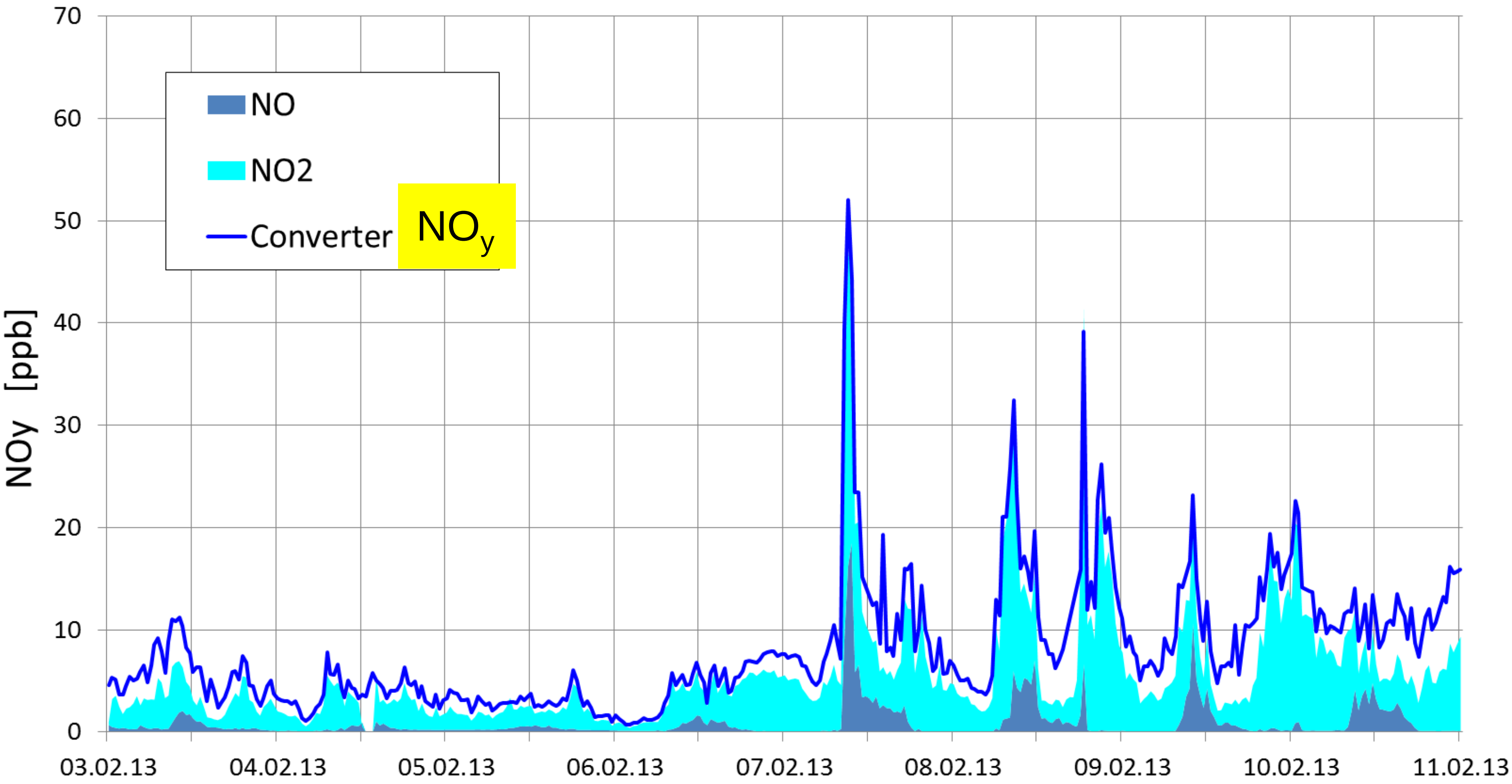
Comparison of $\sum N_r$ converter channel to individual compound measurements

- NO, NO_2: CLD TEI 42C + BLC
- NH_3: Picarro CRDS

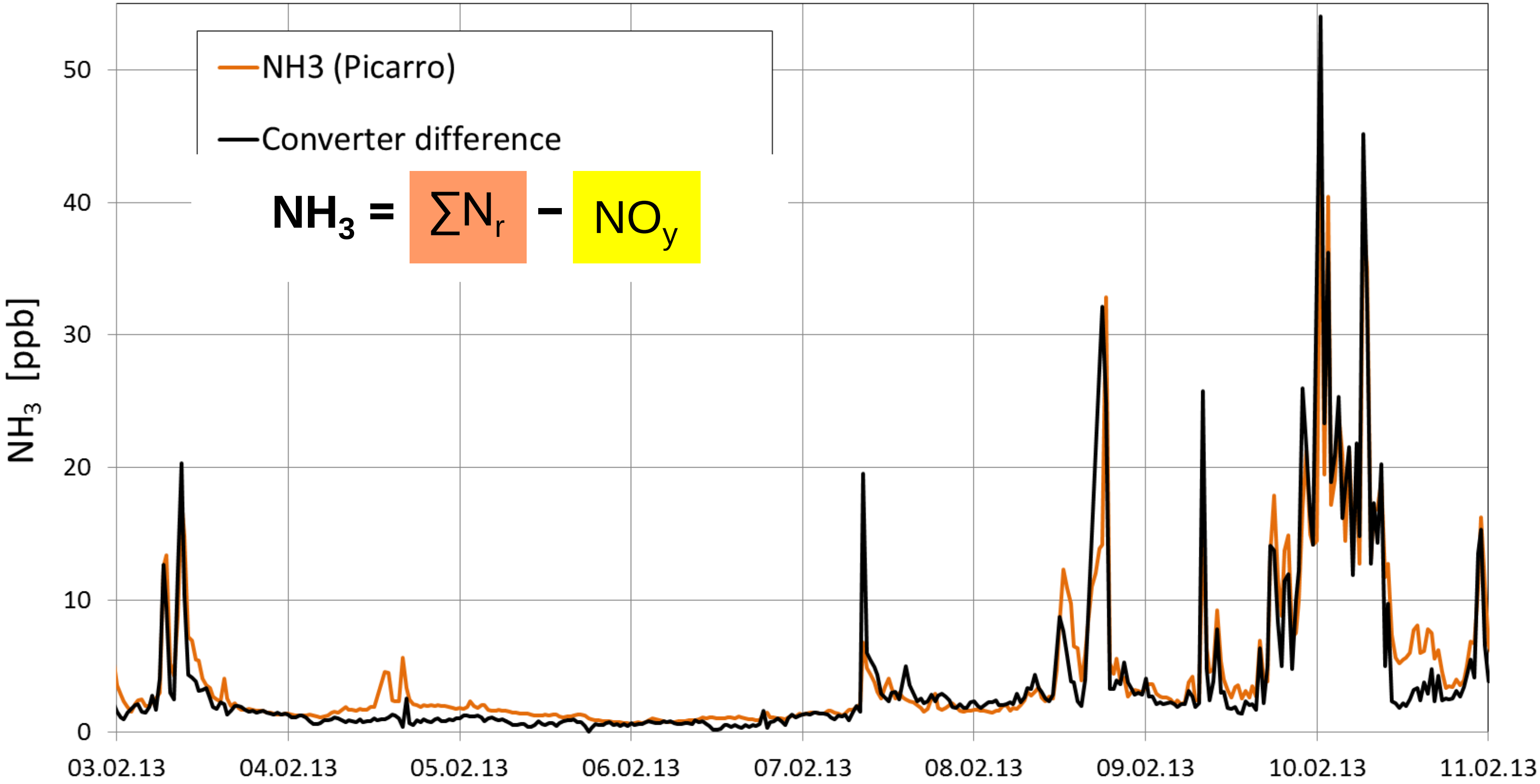


Comparison of NO_y converter channel to individual compound measurements

- NO, NO_2: CLD TEI 42C + BLC



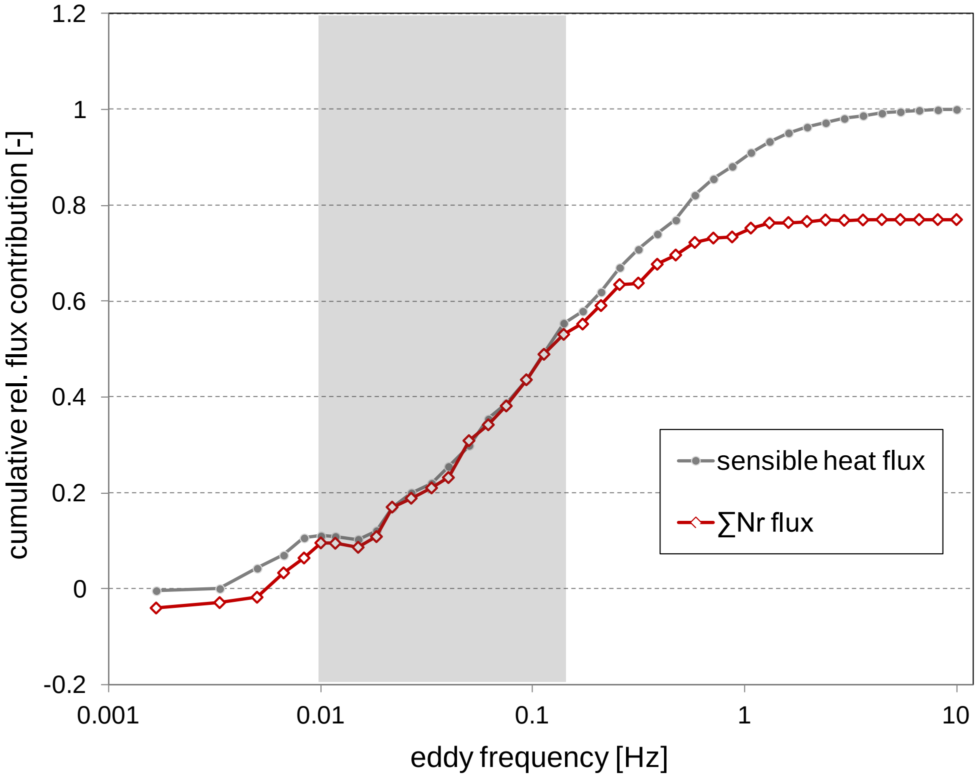
Validation of NH_3 concentration measurements



$$NH_3 = \boxed{\sum N_r} - \boxed{NO_y}$$

Flux quality Issues

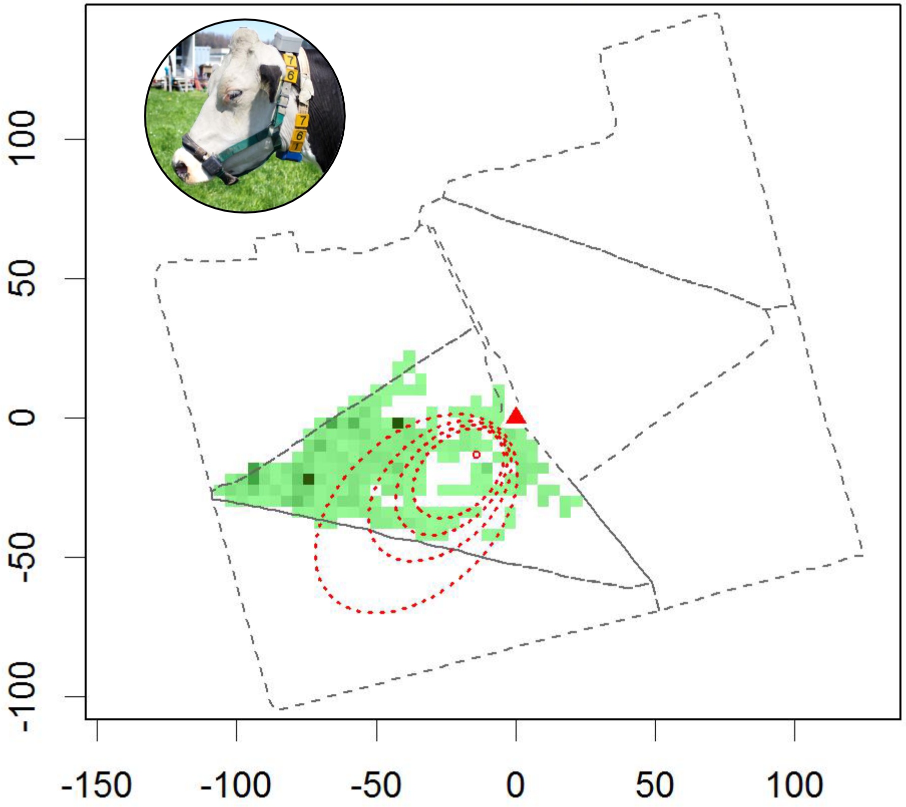
- ❖ A high-frequency damping loss of 15-35% was found depending on stability and windspeed
  → correction based on ogive analysis



- ❖ 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

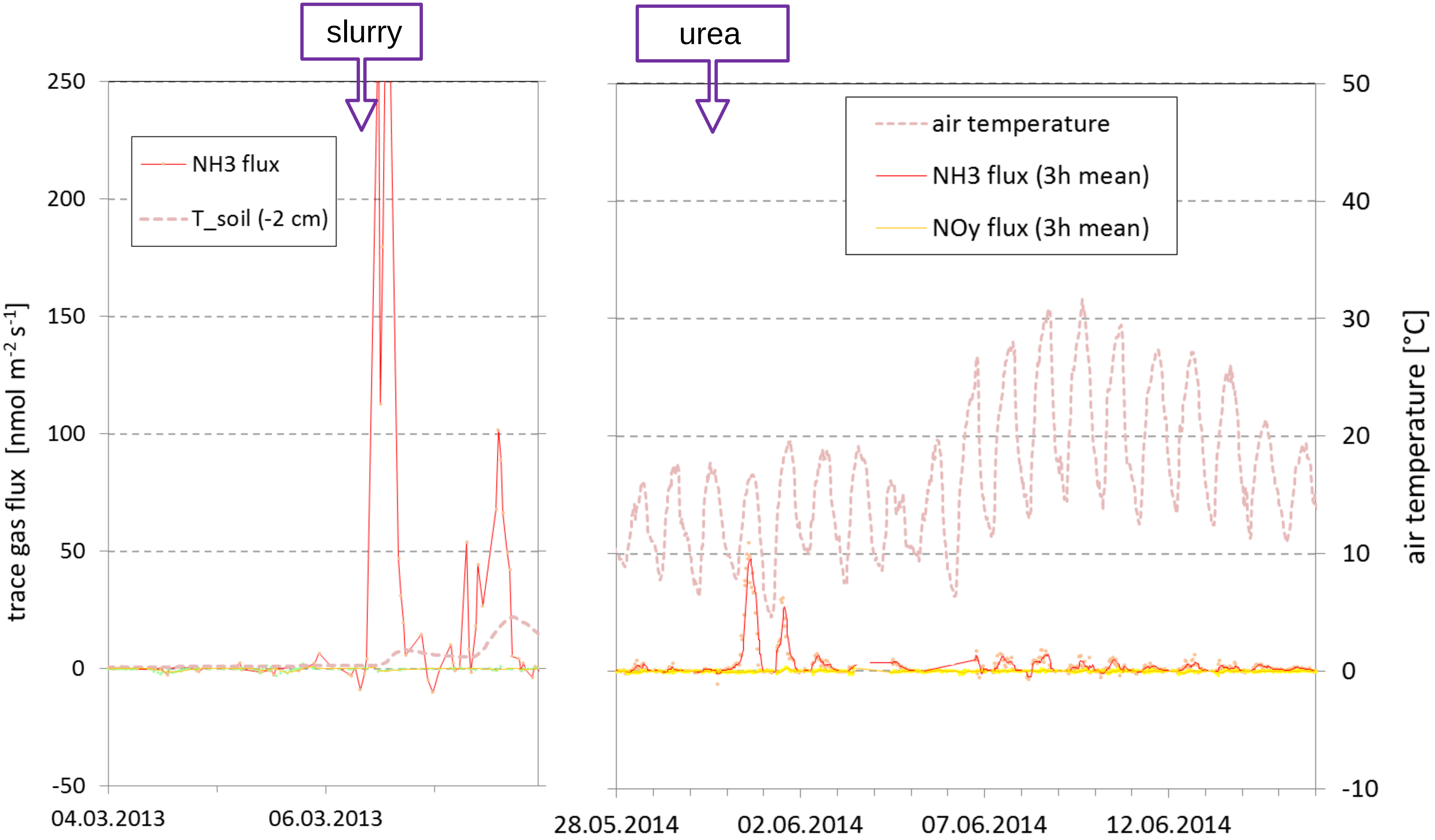
Pasture Site

- 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)



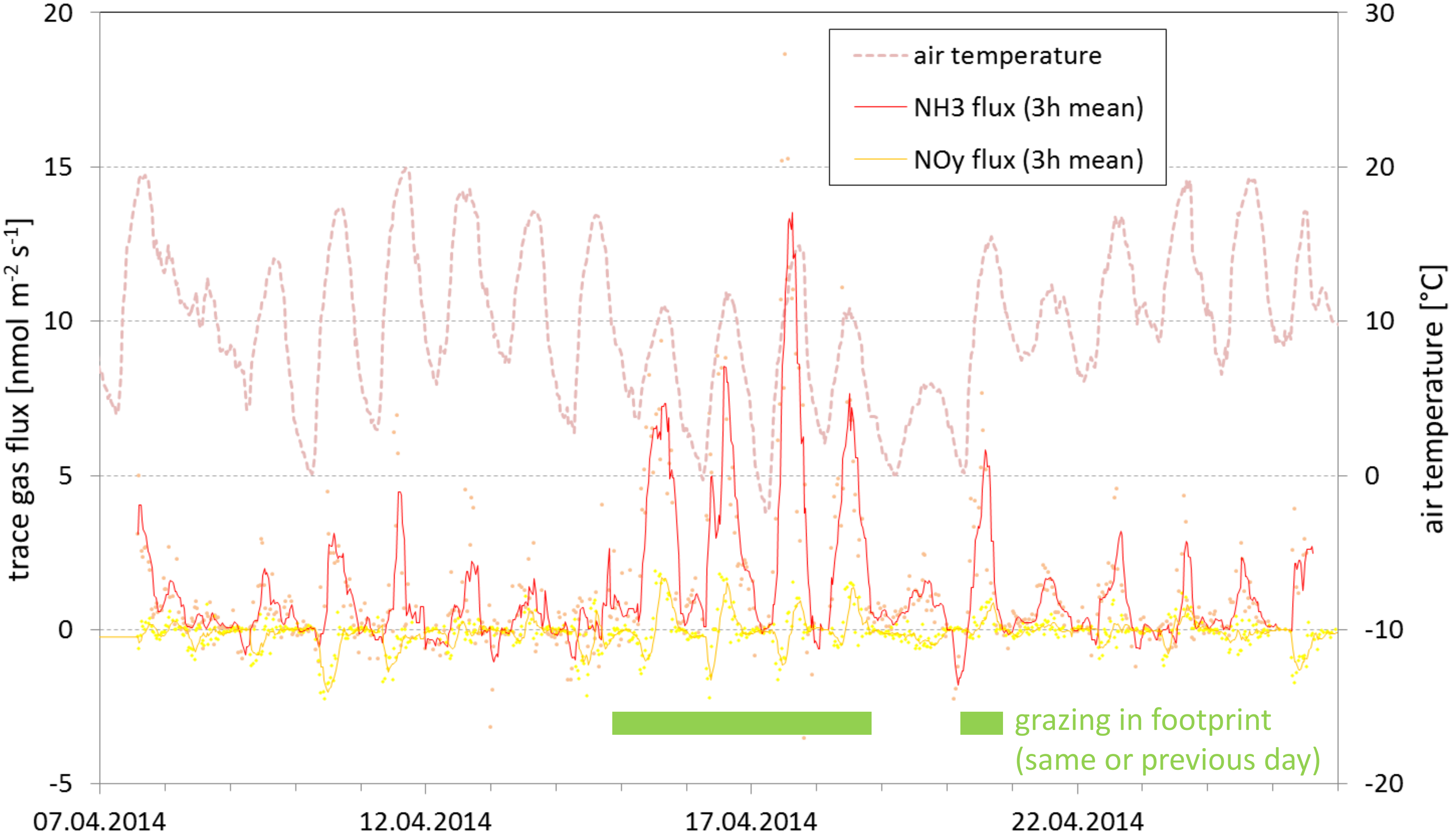
Effect of fertiliser application on NH_3 emission

- Very low temperature during slurry application



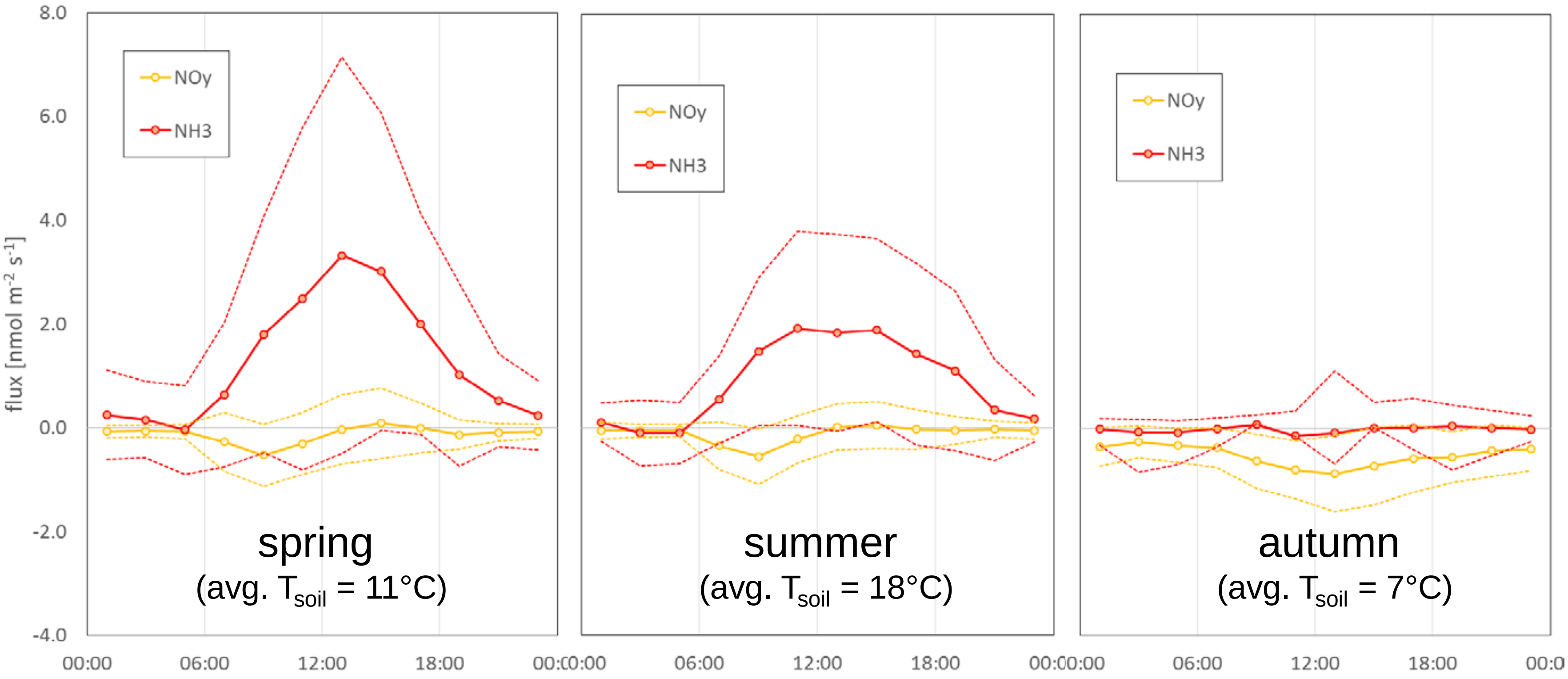
‘Background’ NH_3 flux (grazing season)

- 25 days after last fertiliser application
- in comparison with NO_y exchange



Exchange of NH_3 (background/grazing)

- Mostly (net) NH_3 emissions, highest in spring and lowest in autumn/winter
- Measured NOy flux includes NO emission



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

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 NO_y for NH_3 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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EU-FP7 Project éclaire
&
Swiss Commission for Innovation and Technology
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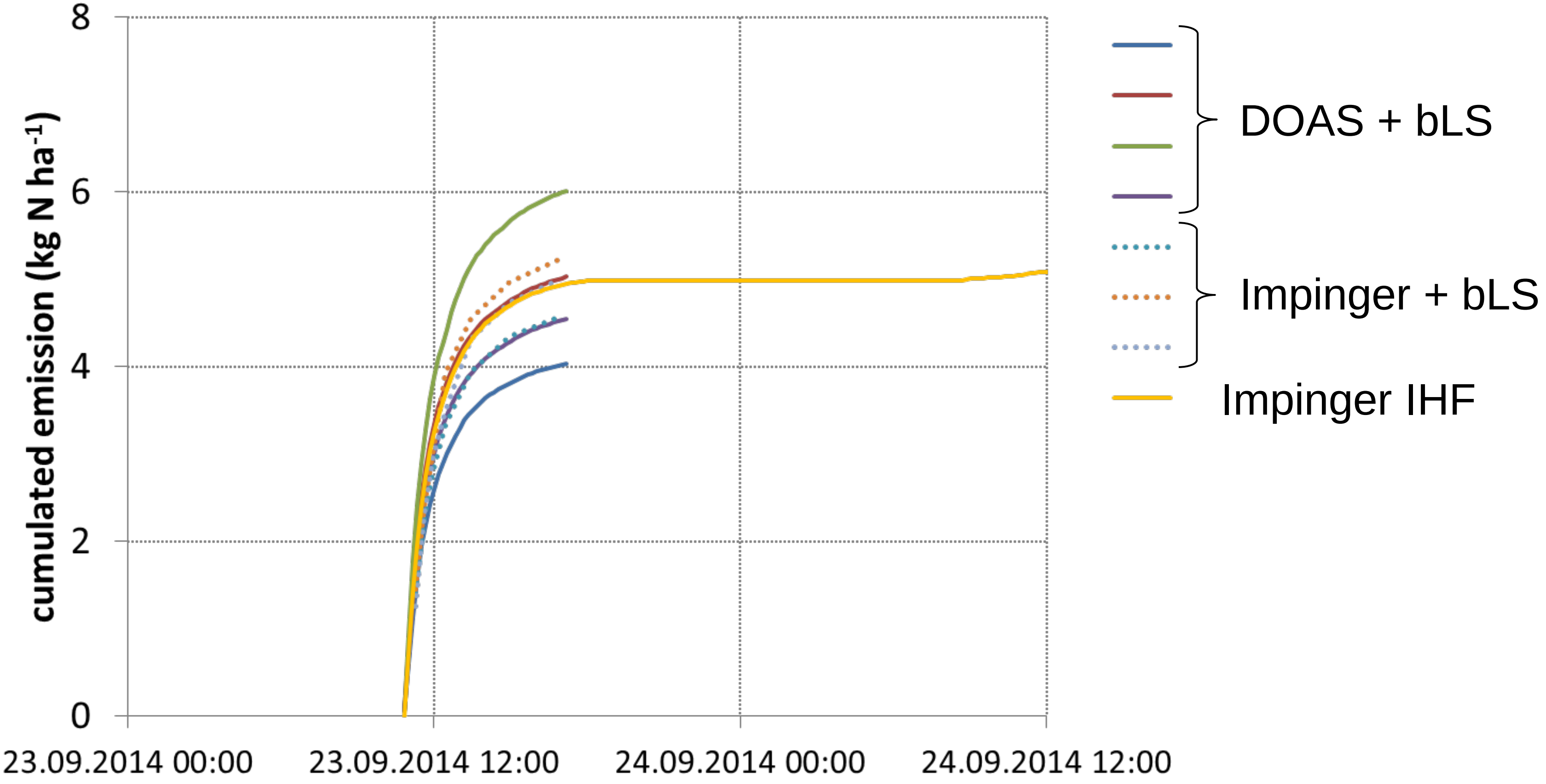
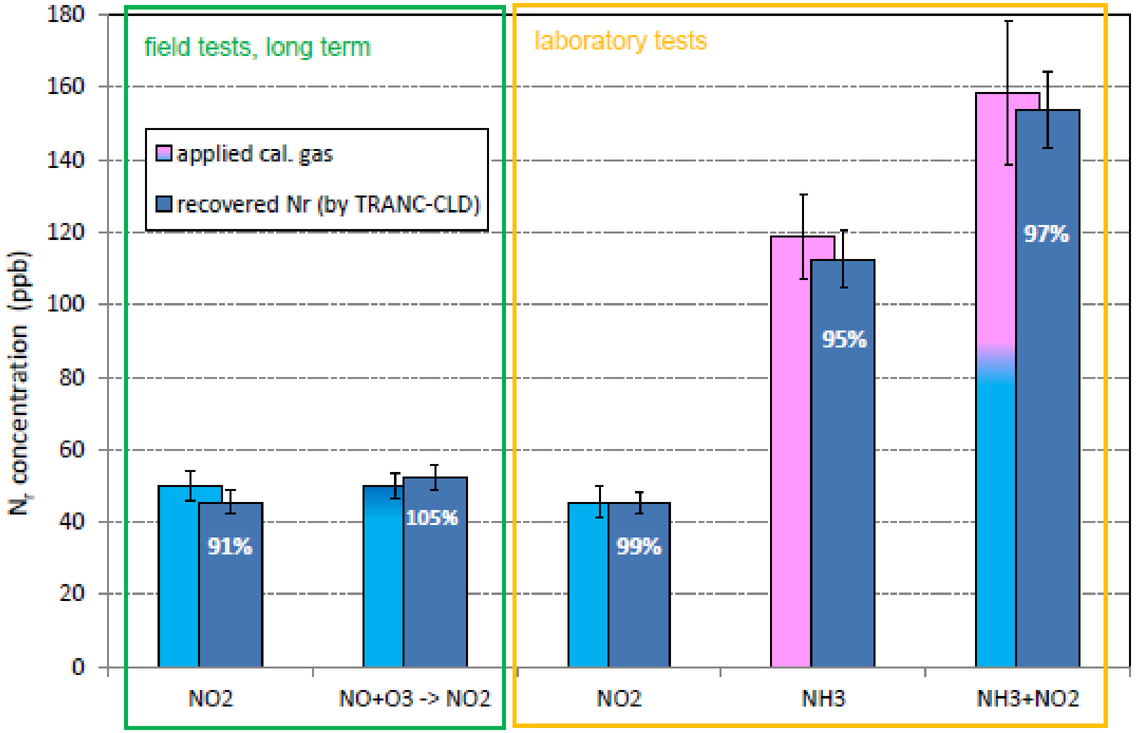
Comparison of bLS and IHF methods



Conversion efficiency tests

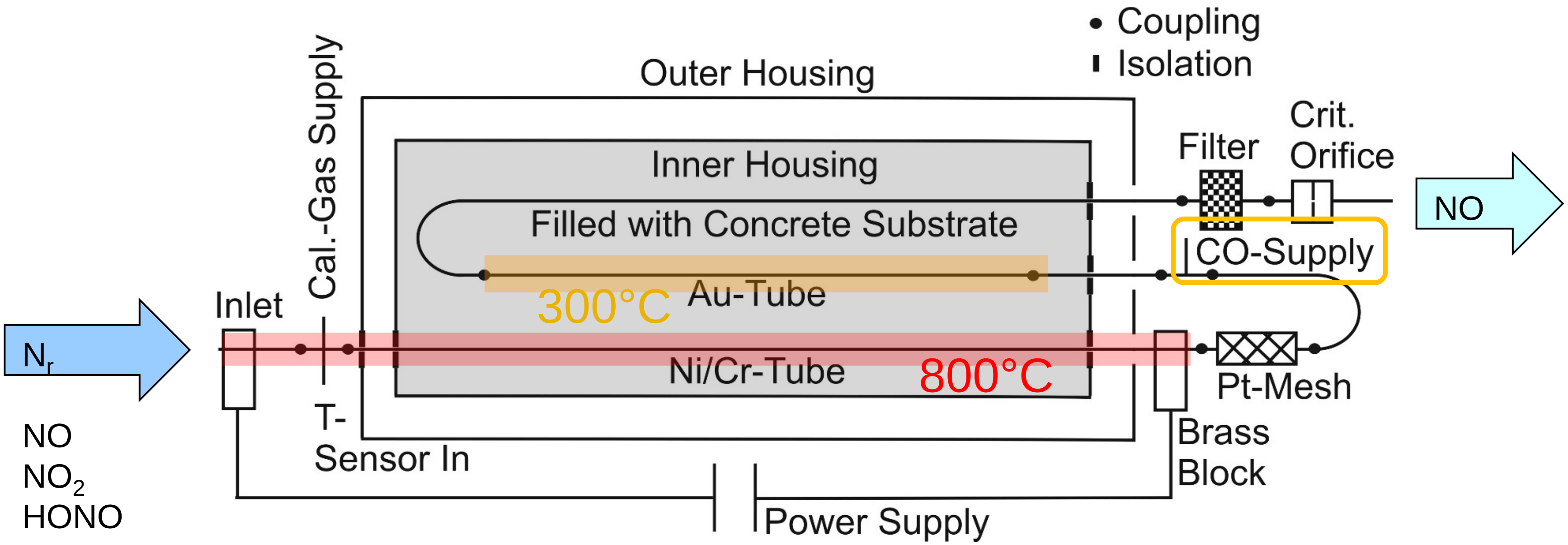
The preparation (mixing) or analysis of calibration gas mixtures for specific components is often problematic and may have a considerable uncertainty



[Marx et al., 2011]

$\sum N_r$ converter principle

Combination of oxidizing and reducing converter



NO
NO_2
HONO
HNO_3
NH_3
particles

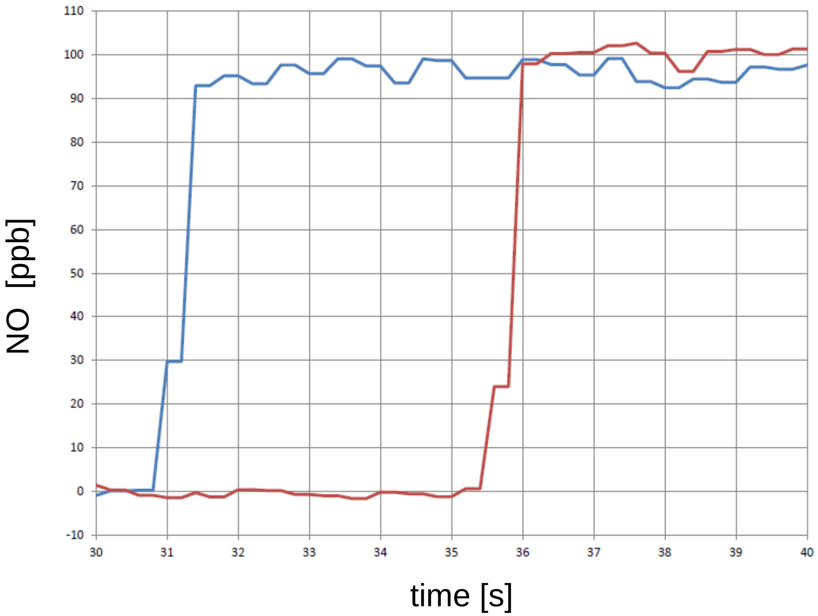
TRANC – a novel fast-response converter to measure total reactive atmospheric nitrogen

O. Marx[1], C. Brümmer[2], C. Ammann[3], V. Wolff[3], and A. Freibauer[2]

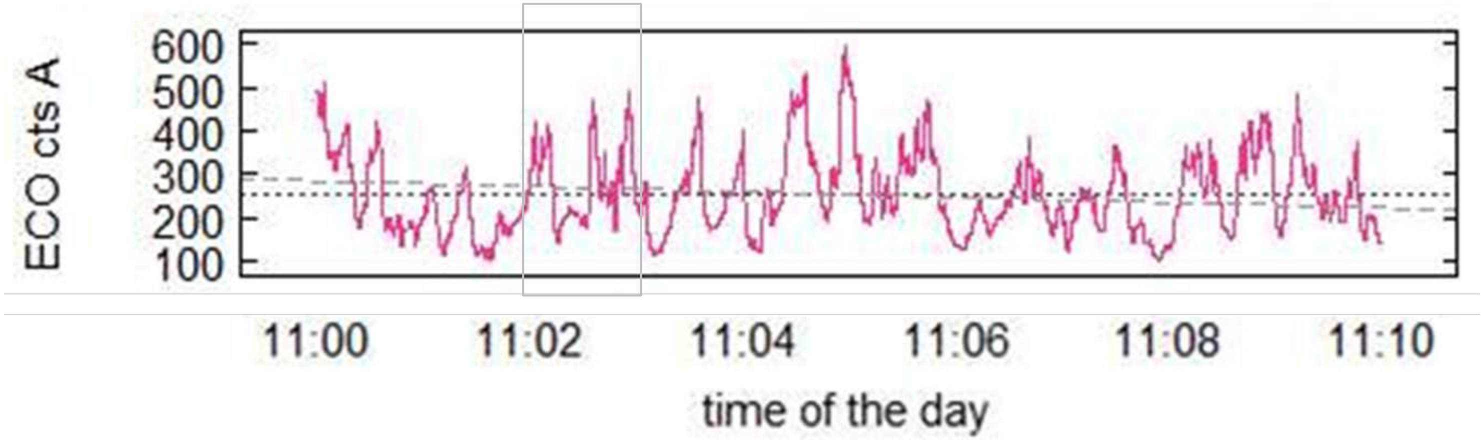
Atmospheric Measurement Techniques

Fast response of NH_3 detection

- ❖ response of NO detector CLD899

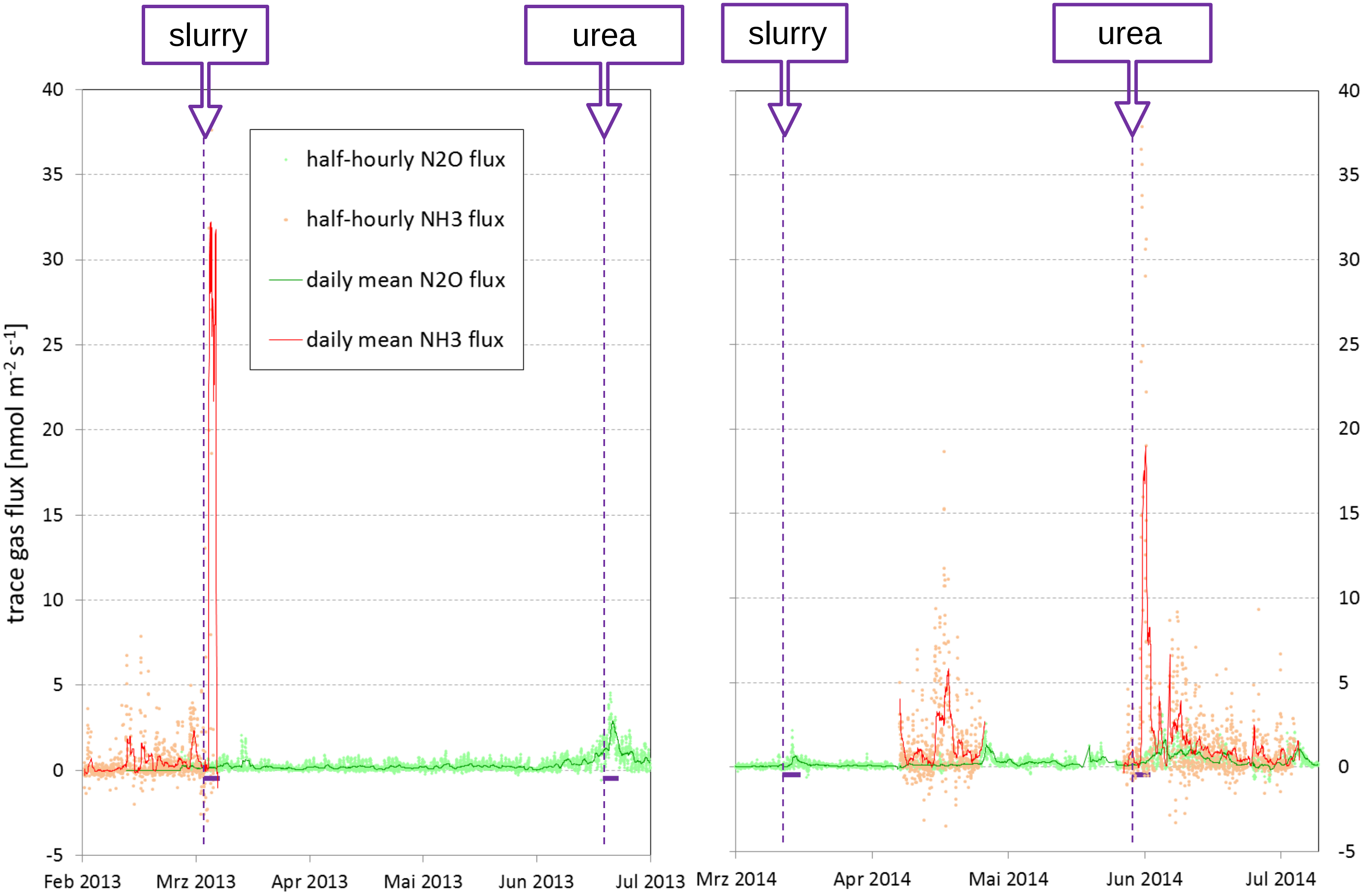


- ❖ $\sum N_r$ channel after slurry application (20 cts ≈ 1 ppb)



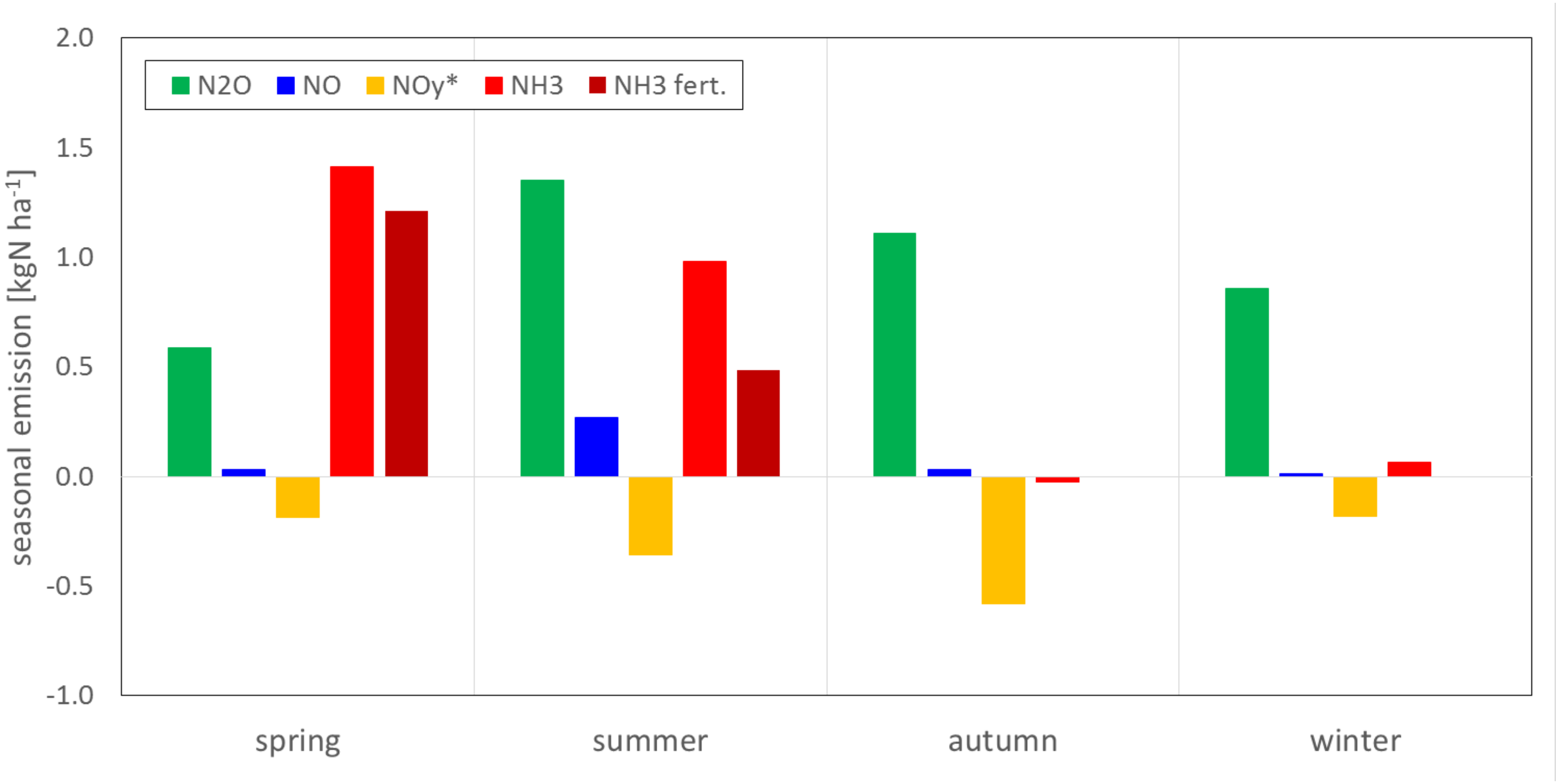
Effect of fertiliser application on NH_3 and N_2O emission

❖ application rates (mineral/TAN): 30-50 kgN ha^{-1}

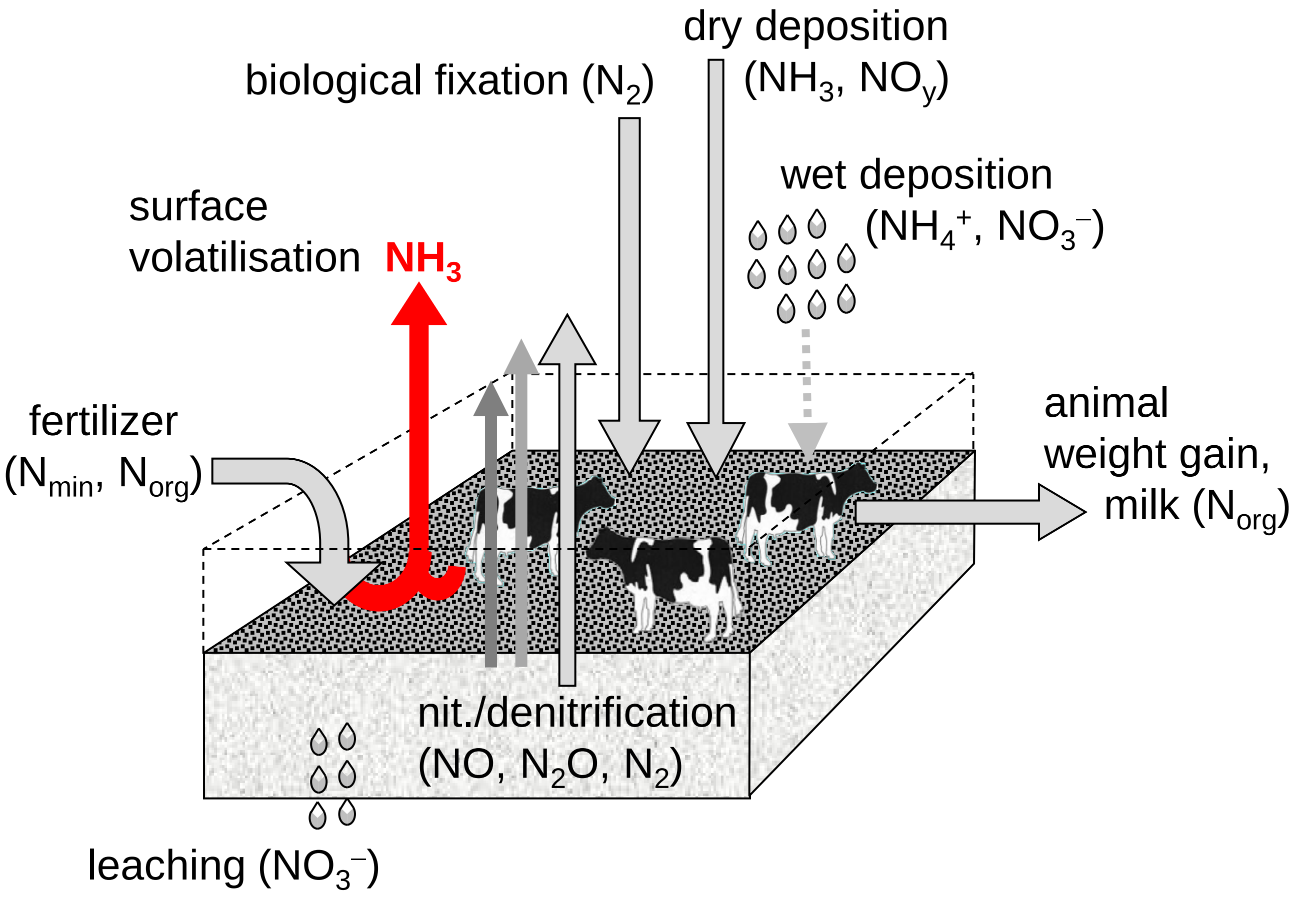


Summary of reactive N gas exchange (year 2013)

- Simple upscaling of mean diurnal cycles to seasonal emissions
- Similar importance of fertilizer application events and background emissions for NH_3 (in contrast to NO and N_2O)
- Strong seasonality for NO and NH_3 emission, but not for N_2O emissions



Motivation I: Nitrogen budget and gaseous emissions of pasture with grazing animals



Concentrations and EC fluxes of NO and NO_2

Agroscope

Measurement method: Eddy Covariance (EC)

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