NitroEurope IP

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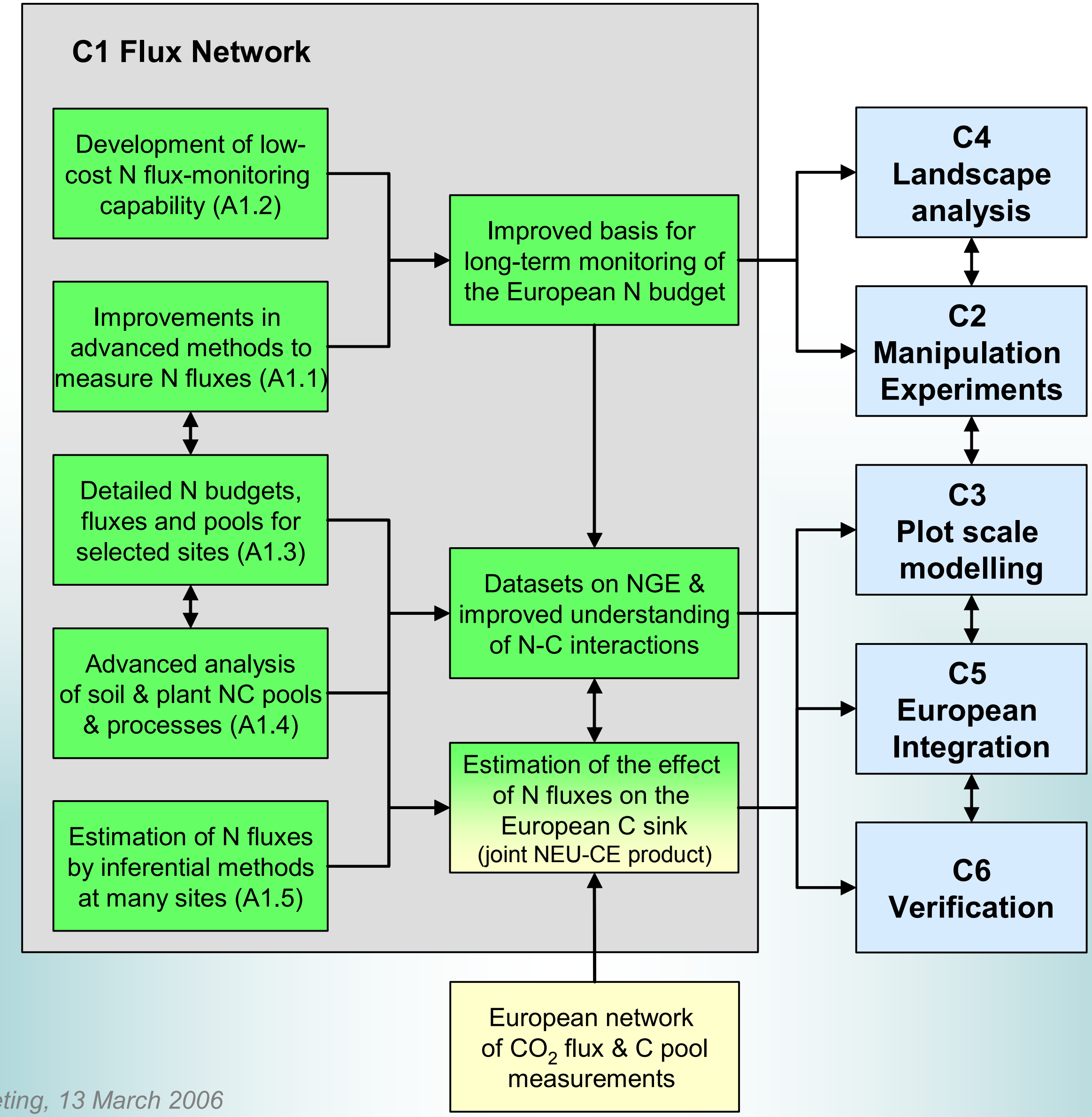
Overview of flux measurement techniques for reactive nitrogen and greenhouse gases

Eiko Nemitz, CEH Edinburgh

NitroEurope Component 1

- Level 3 (13 "Super Sites"): N and GHG fluxes: Core Measurements + Special Topics. Includes high cost micrometeorological methods, auto-chambers with online chemical analysis and *process studies*.
- Level 2 (9 "Regional Sites"): Basic N and GHG flux monitoring to get *annual budgets*, e.g. COTAG, simple cuvettes
- Level 1 (~50 "Inferential Sites"): Basic N air concentration measurements at existing CO_2 flux sites for *deposition estimates* by inferential modelling

Structure of Component 1



Contents

- **Monthly monitoring techniques (Level 1)**
  - The DELTA denuder
- **Time-averaged flux techniques (Level 2)**
  - The Time Averaged Gradient (TAG) technique
- **High time resolution network flux techniques (Level 3)**
  - Examples from previous projects covered in the next talk (Ute Skiba)
- **State-of-the-art advanced flux measurement techniques (Level 3 – Special Topics)**
  - Fast chamber techniques
  - Continuous gradient systems for reactive gases and aerosols (GRAEGOR)
  - Eddy-covariance system for (NO_3^-) aerosol
  - Use of TDL-AS for eddy-covariance flux measurements of CH_4, N_2O, NH_3 (and HNO_3)
  - Eddy-covariance system for organic nitrogen based on CIMS

Level 1: Monthly Concentration Monitoring - The DELTA Sampler

Long denuders 1+ 2
To remove HNO_3, SO_2 and HCl; K_2CO_3 coated

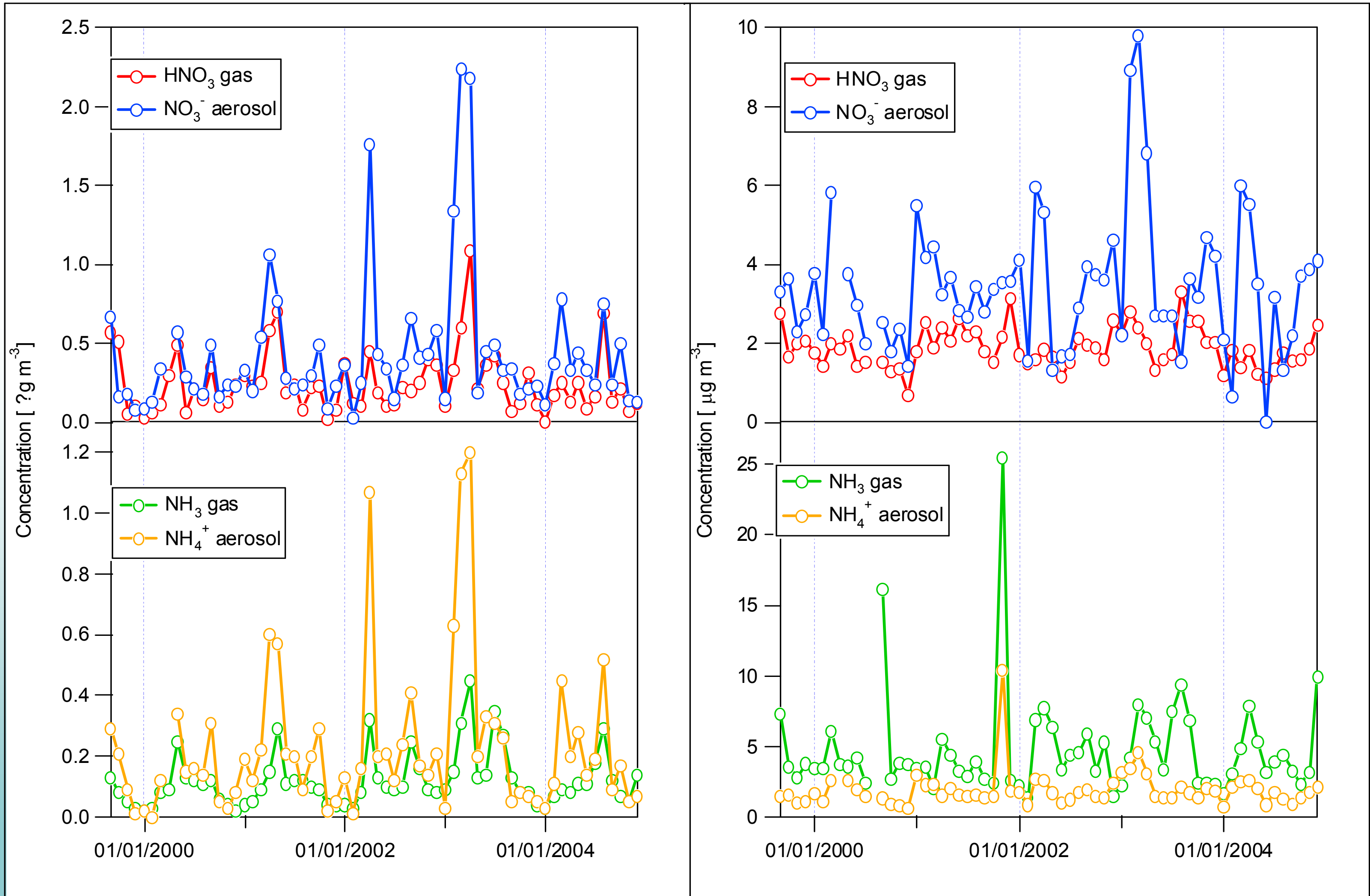
Shorter denuders 3 + 4
To remove NH_3
Citric acid coated

Aerosol filter
To remove particulate NH_4^+, NO_3^-, SO_4^{2-}, Cl^-, and base cations Na^+, Ca^{2+}, Mg^{2+}

Example Time Series

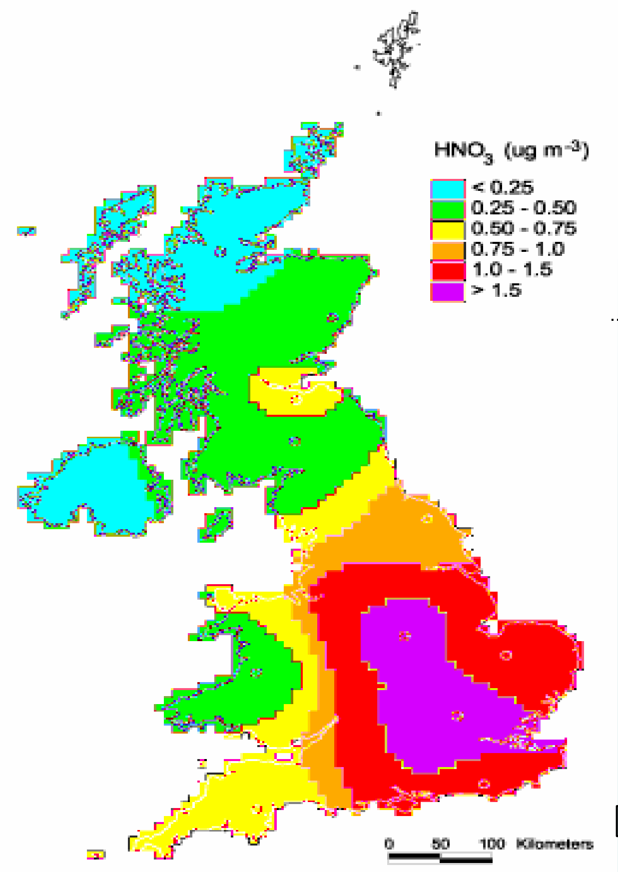
Strathvaich Dam
Remote Scottish Upland Site

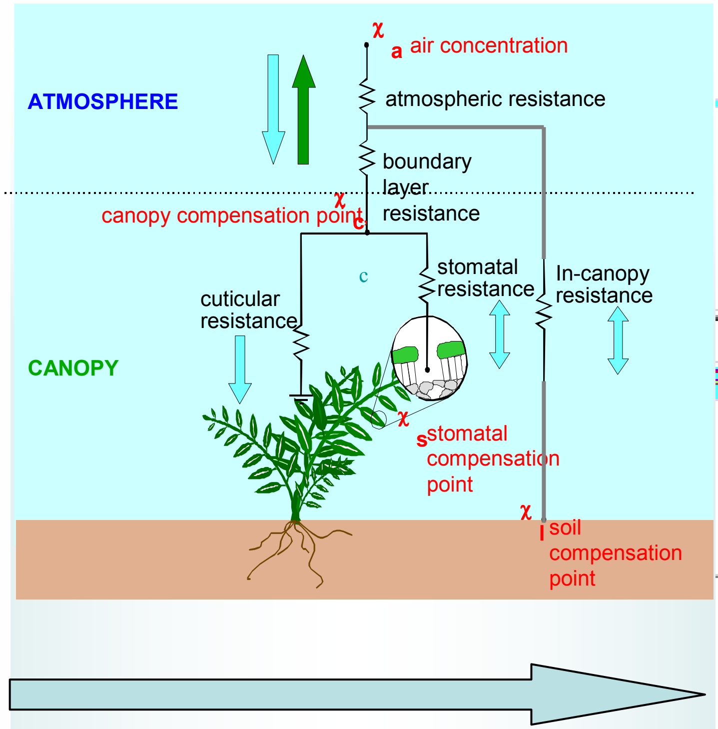
Sutton Bonnington
SO_2 Source Region



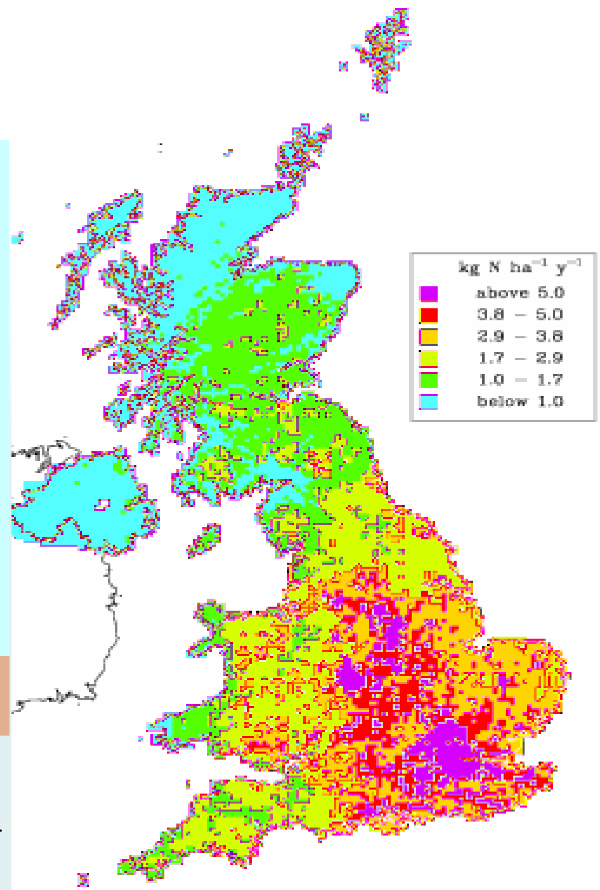
Inferential approach to derive deposition from monitored concentrations

HNO_3 air concentration





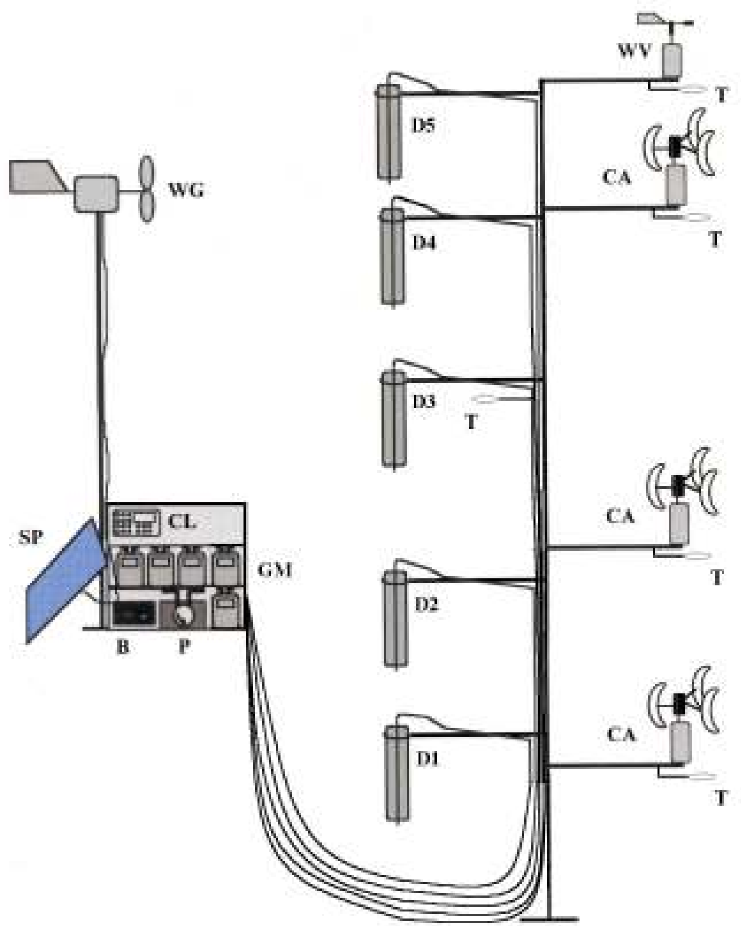
HNO_3 dry deposition

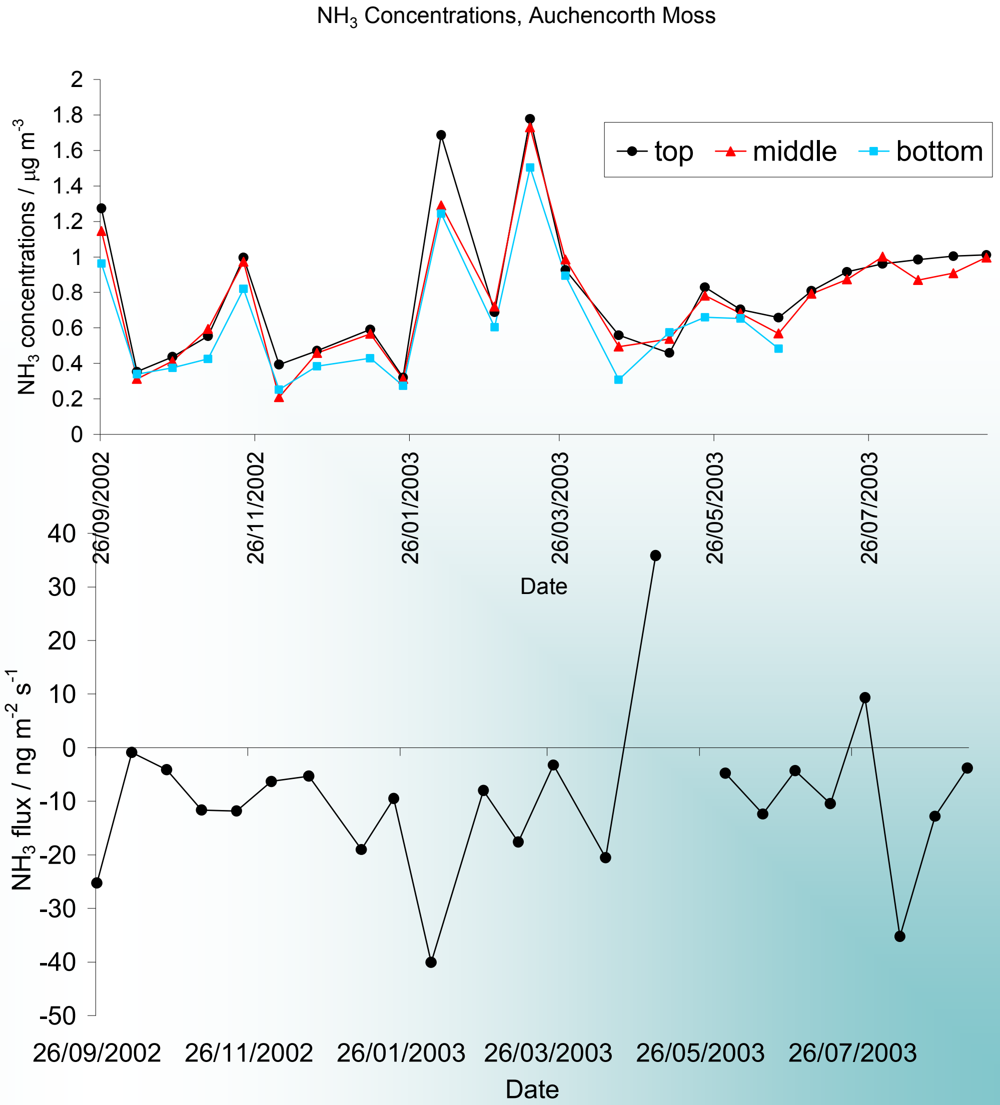


Level-2 low-cost flux measurement technology

- Systems to be developed
  - Long-term flux chamber (Level-2 sites)
    - CEH
    - RISO
  - Long-term flux system for reactive gases and aerosols (Level-2 & Level-3 sites)
    - ECN & TNO (Time Averaging Gradient or REA system)
    - CEH & UoE (Time Averaging Gradient or REA system)
    - UoZ (photo-acoustic NH_3 sensor)
  - Low cost assay for N_2 fixation (Level-2 sites)
    - RISO
- Time scale
  - Development over 18 months.
  - Best system goes into production
    - Any system can be considered
    - Funds for production currently in reserve (not allocated)
  - Instrumentation runs from year 3.

The Time Averaged Gradient (TAG) Approach





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Level-3 techniques
How well can we measure N fluxes?

Gold standard: Eddy covariance

Easy — Difficult

CO_2 CH_4 N_2O NO_2 aerosol N PAN NH_3 HNO_3

Silver standard: Gradient methods

Easy — Difficult

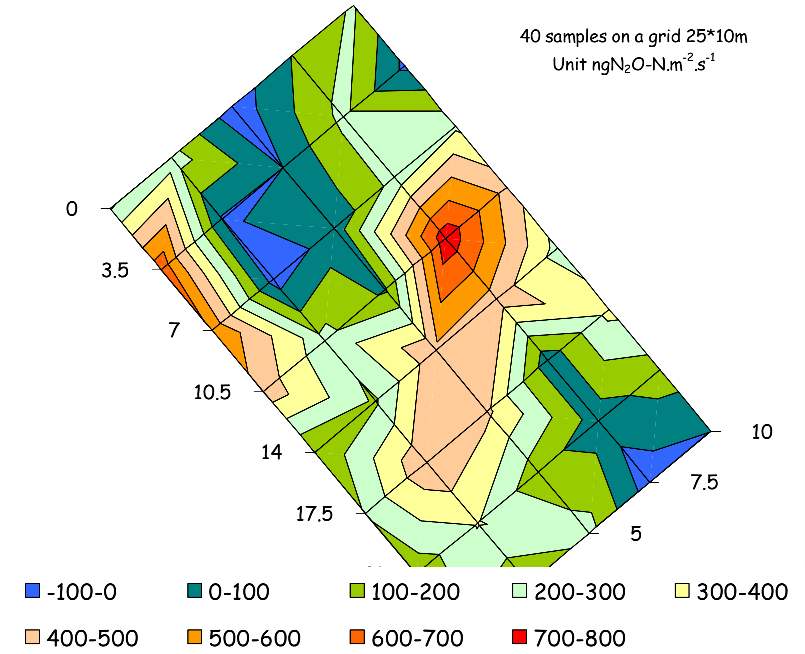
NO_2/O_3 NH_3 HNO_3 aerosol N org. N

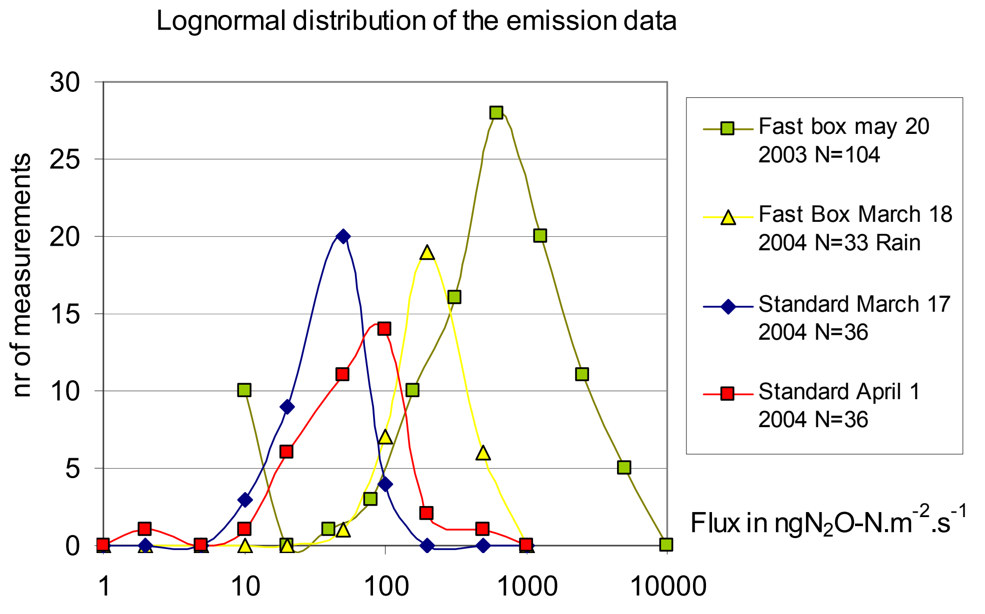
Bronze standard: Chamber methods

Easy — Difficult

N_2O CH_4 NO_2 NH_3 HNO_3

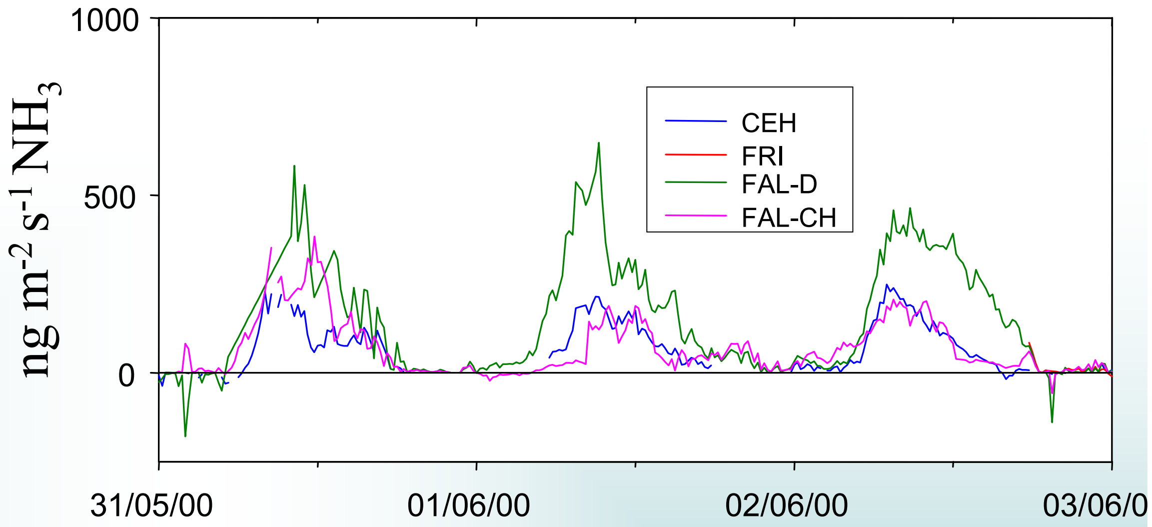
Fast Box Technique for N_2O (ECN)



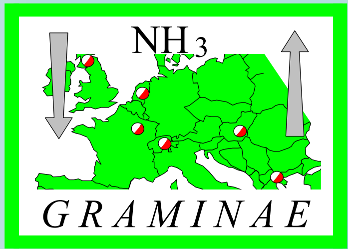


Spatial variability of N_2O fluxes measured with the fast box technique at Lelystad (The Netherlands), and log-normal distribution of measured fluxes (unit: ng N_2O-N m^{-2} s^{-1}).

Continuous gradient measurements for NH_3 fluxes by wet chemistry

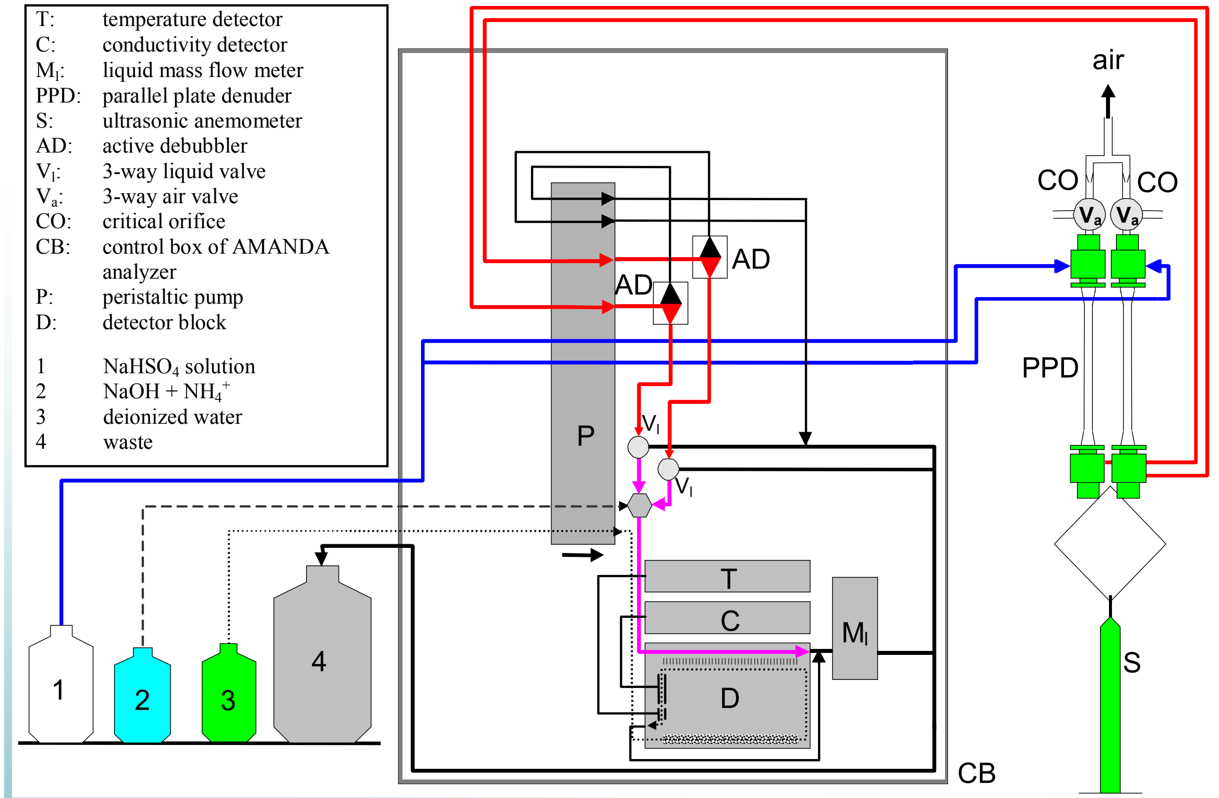


FAL Braunschweig

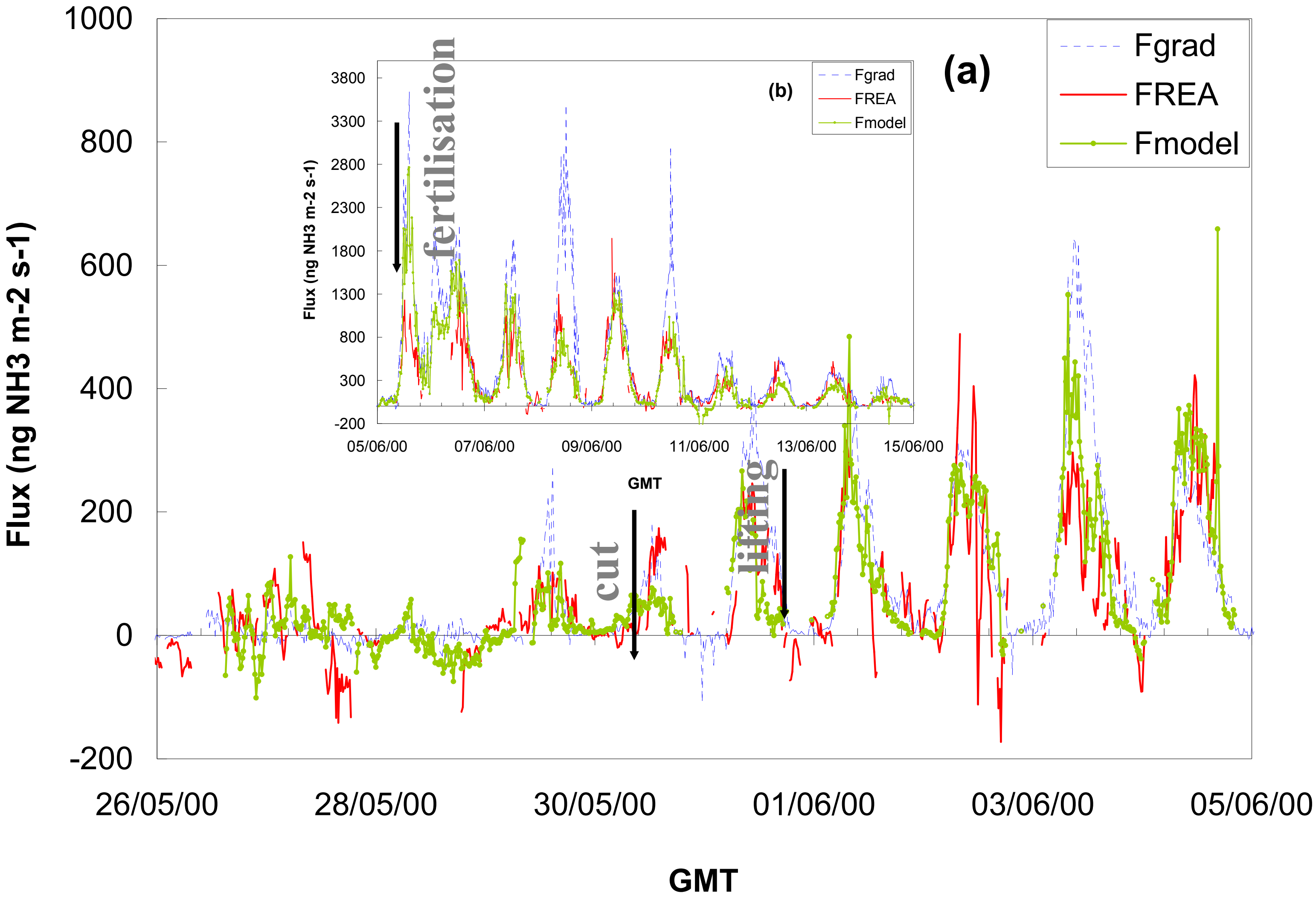


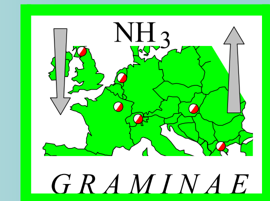
- Current state-of-the-art
- Suitable for long-term measurement
- Very labour intensive
- Inter-comparison shows significant scatter

Continuous relaxed eddy accumulation (REA) systems for NH_3

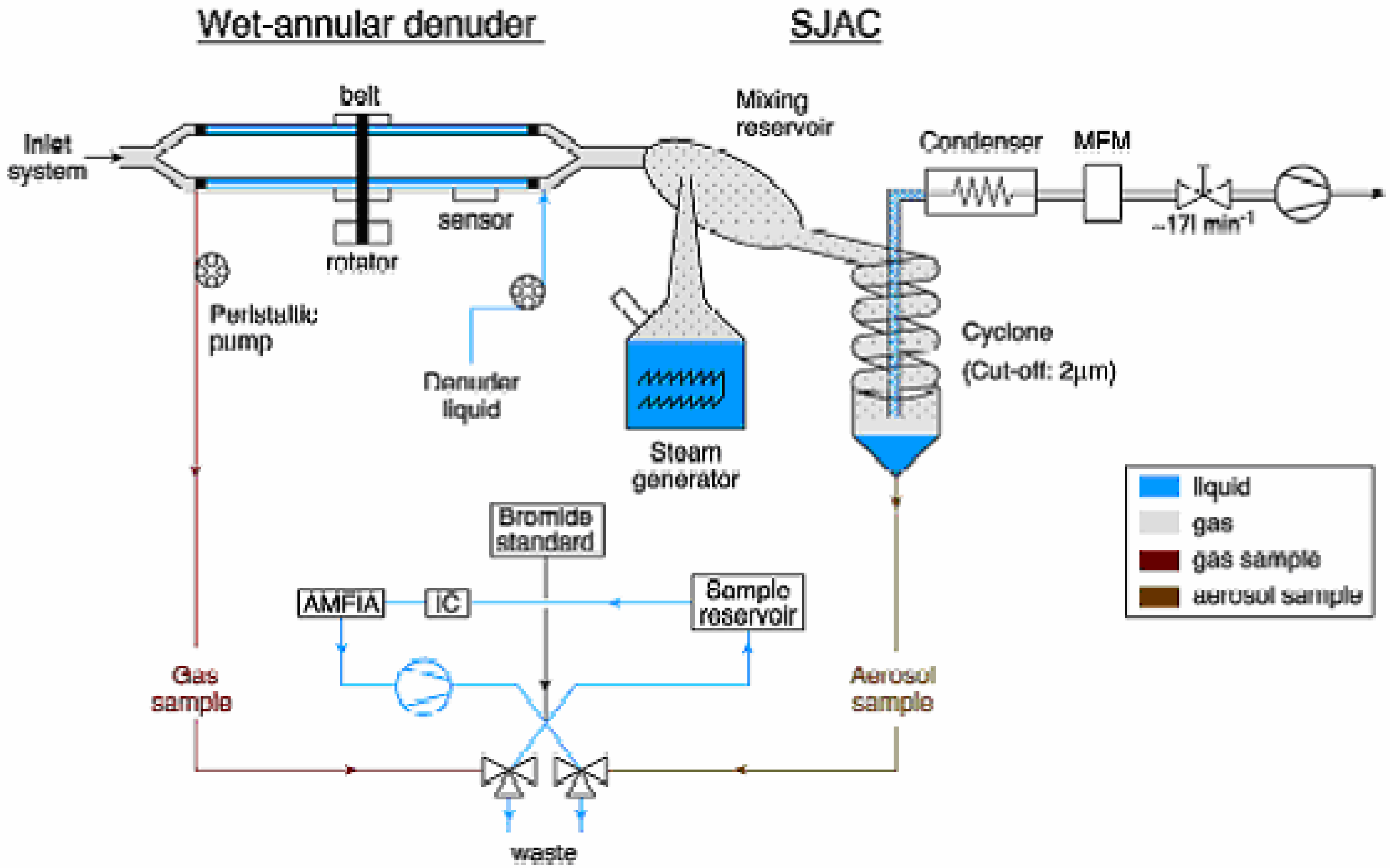


Comparison of the REA system with other techniques

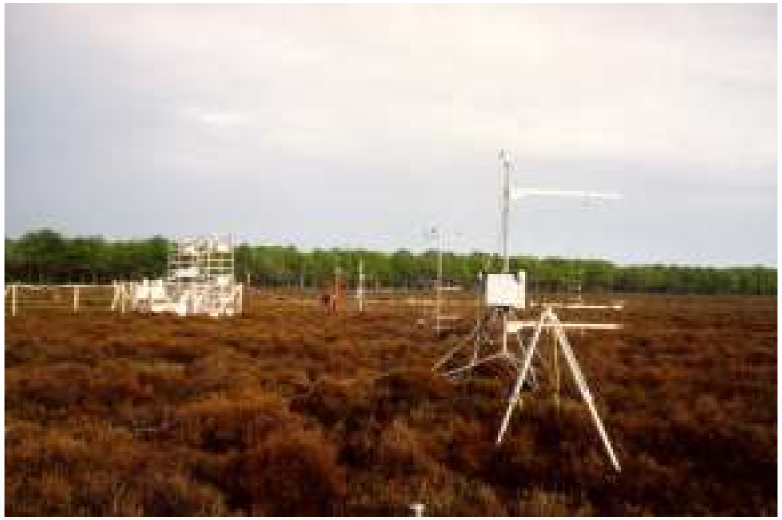


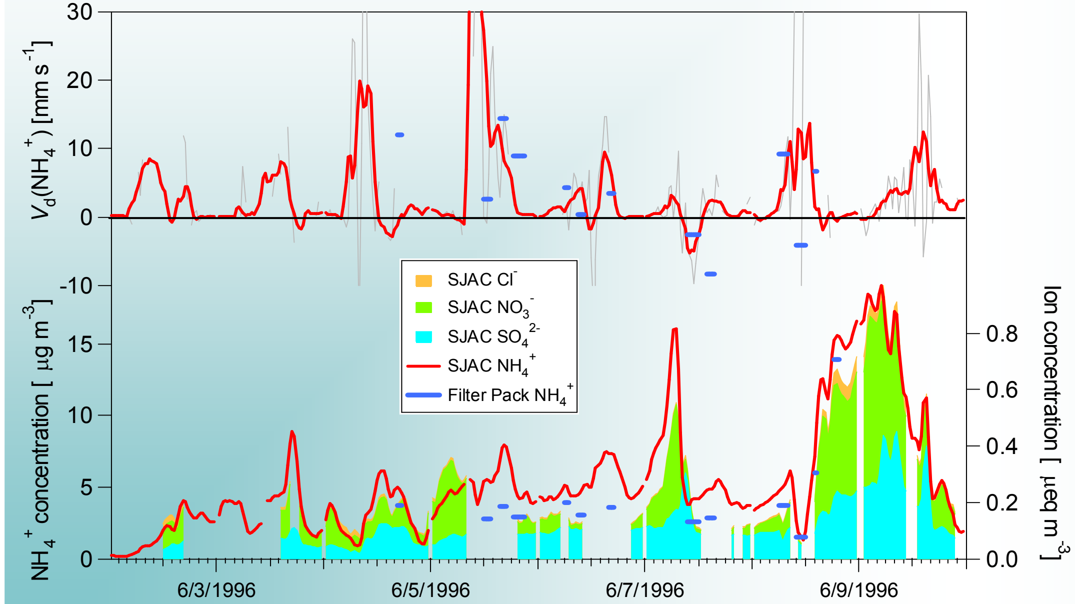


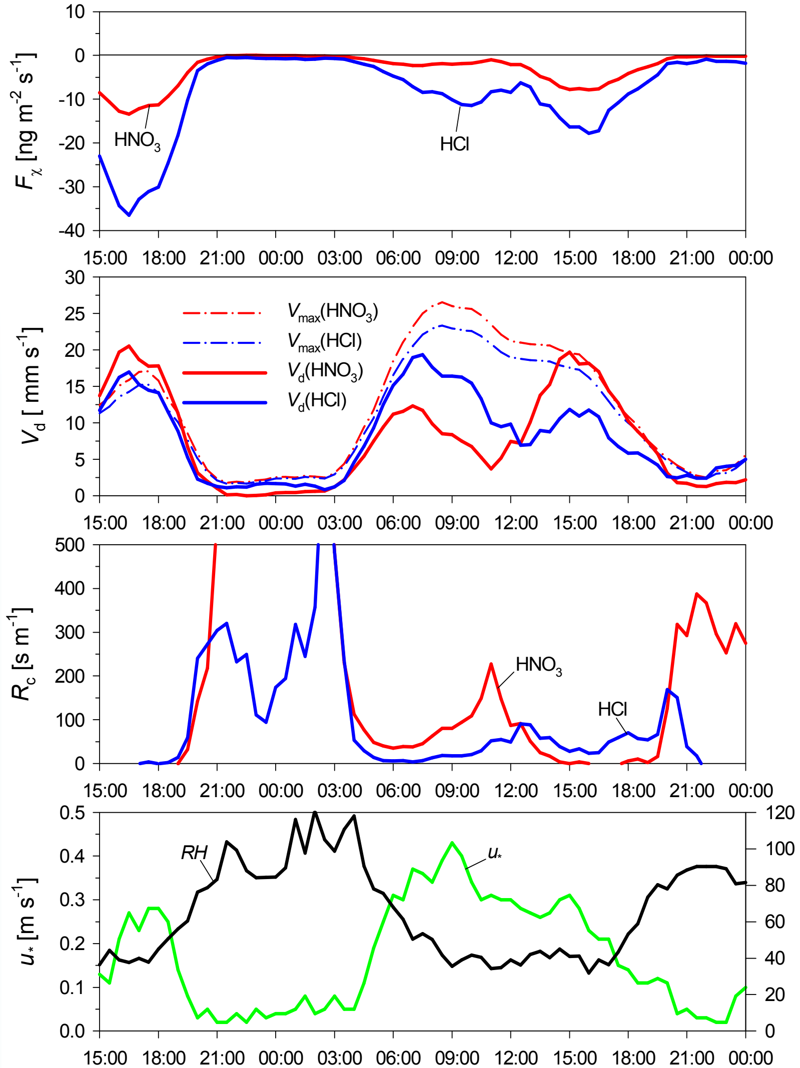
Gradients of Reactive AErosols and Gases with Online Registration (GRAEGOR)



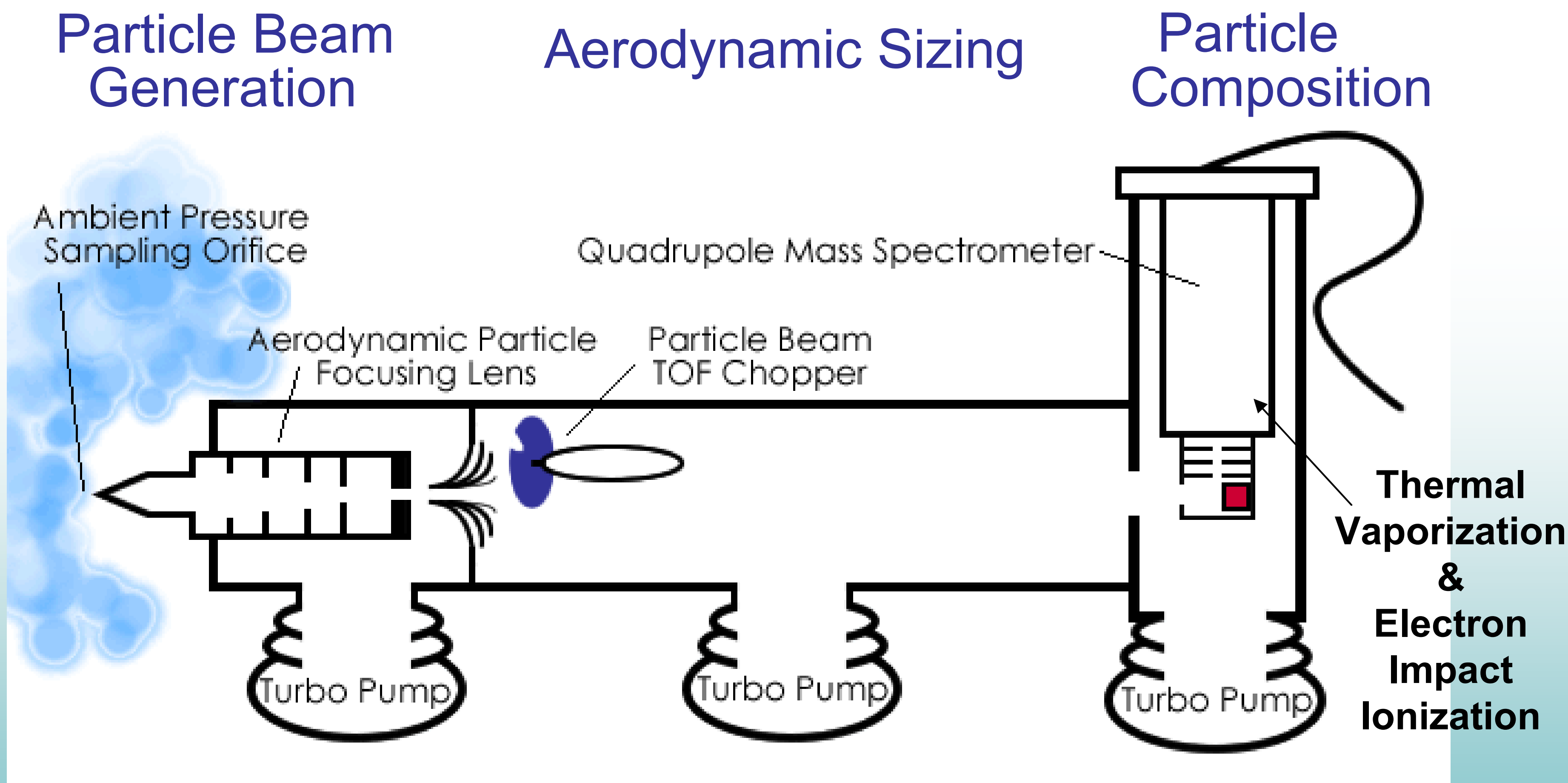
Exchange of Aerosols and Acids over Heathland







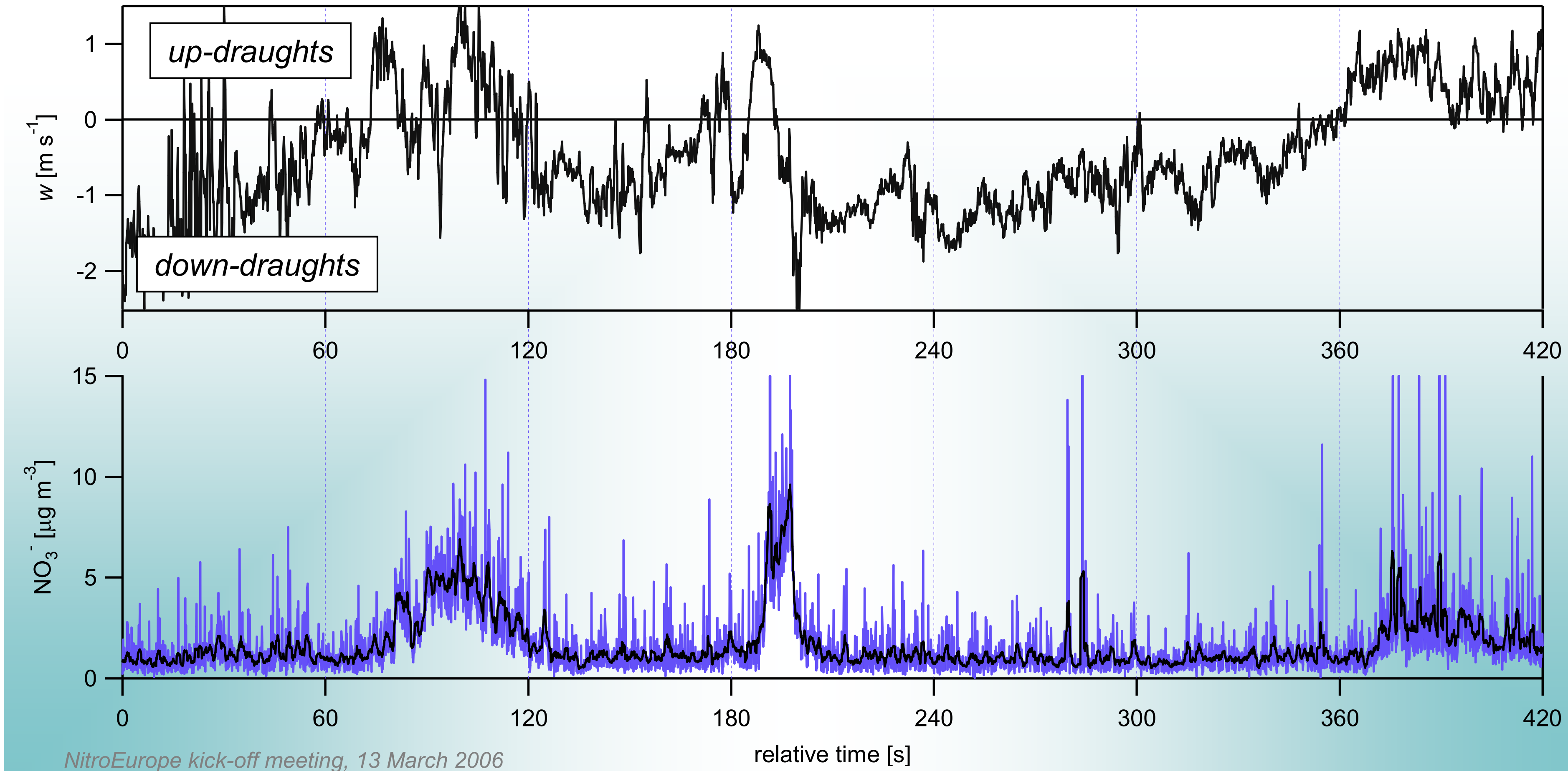
The Aerodyne Aerosol Mass Spectrometer (AMS)



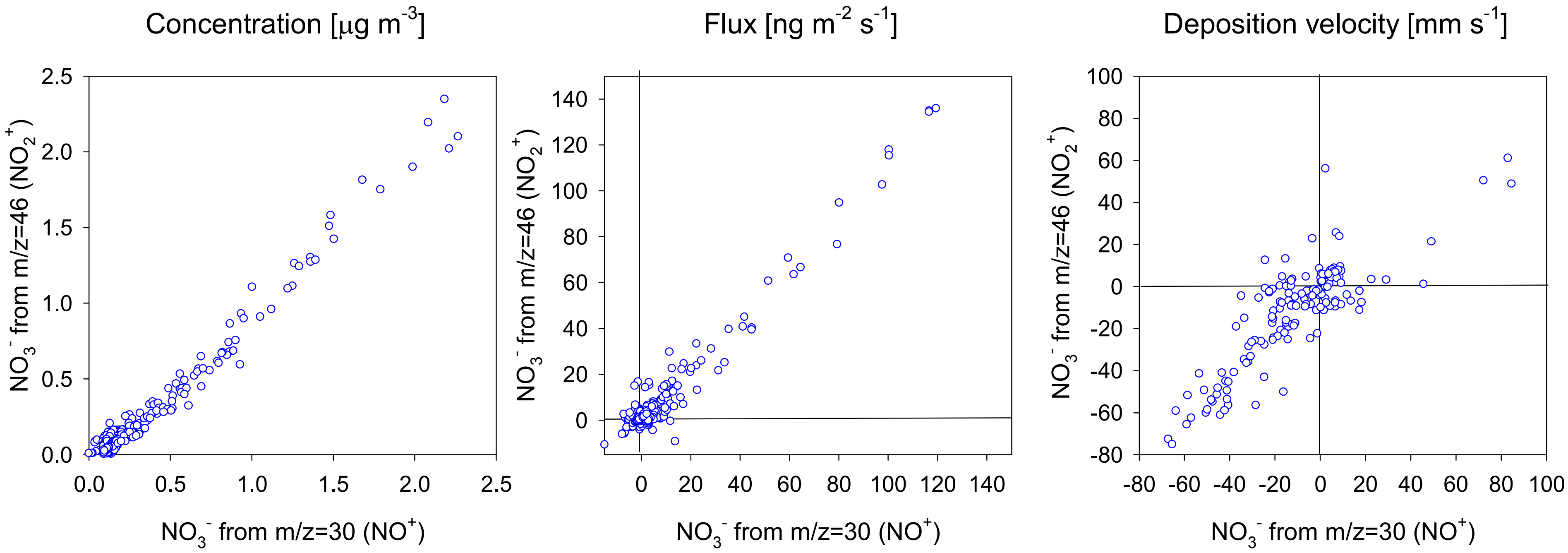
Jayne *et al.*, *Aerosol Science Technology* **33**:1-2(49-70), 2000.

Example Time-Series Measured with AMS (Urban Emission of NO_3^-)

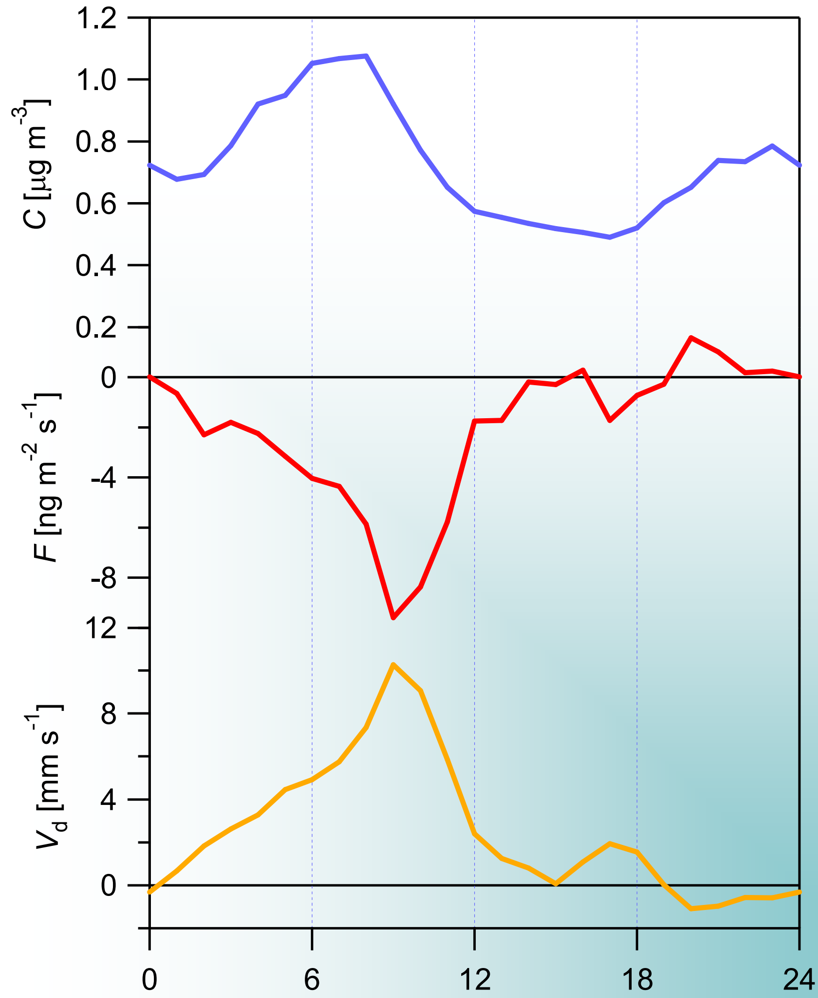
$$F_N = \overline{w'\chi'_N} = \overline{w\chi_N} - \overline{w}\ \overline{\chi_N}$$



Nitrate Comparison (above a City)



Averaged diurnal cycles of NO_3^- fluxes over a pine plantation



Observations of Aerosol Nitrate Emissions above Urban Areas

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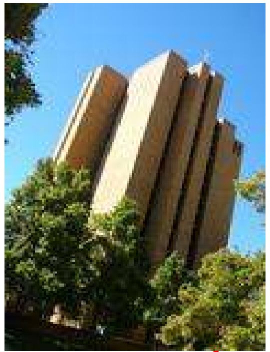
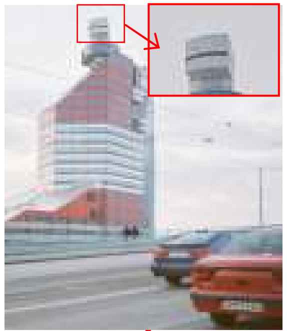
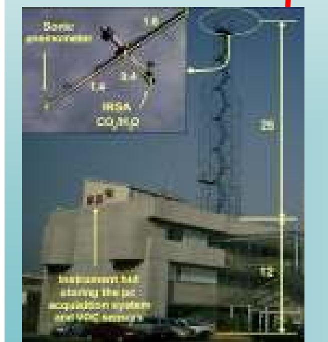


Boulder, CO
(80,000)

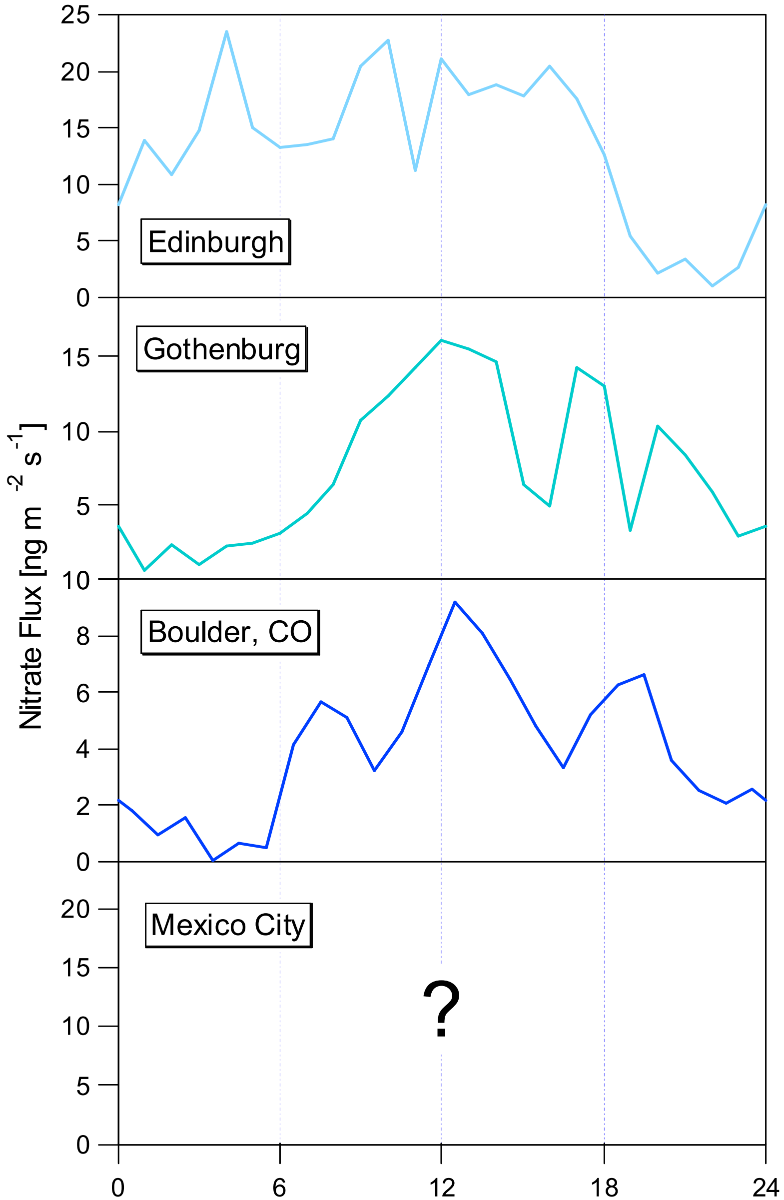
Gothenburg
(480,000)



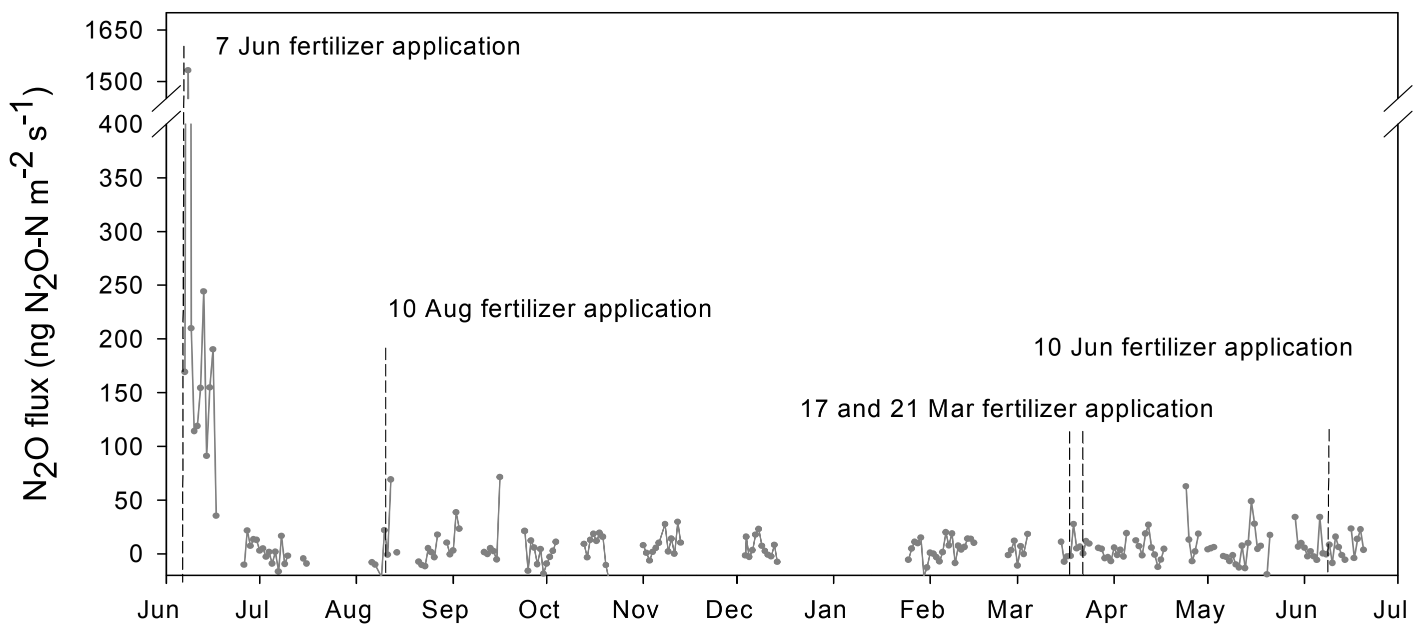


Mexico City
(20,000,000)

Edinburgh
(435,000)



Field scale N_2O flux measurements



First Intercomparison of TDL-AS for NH_3

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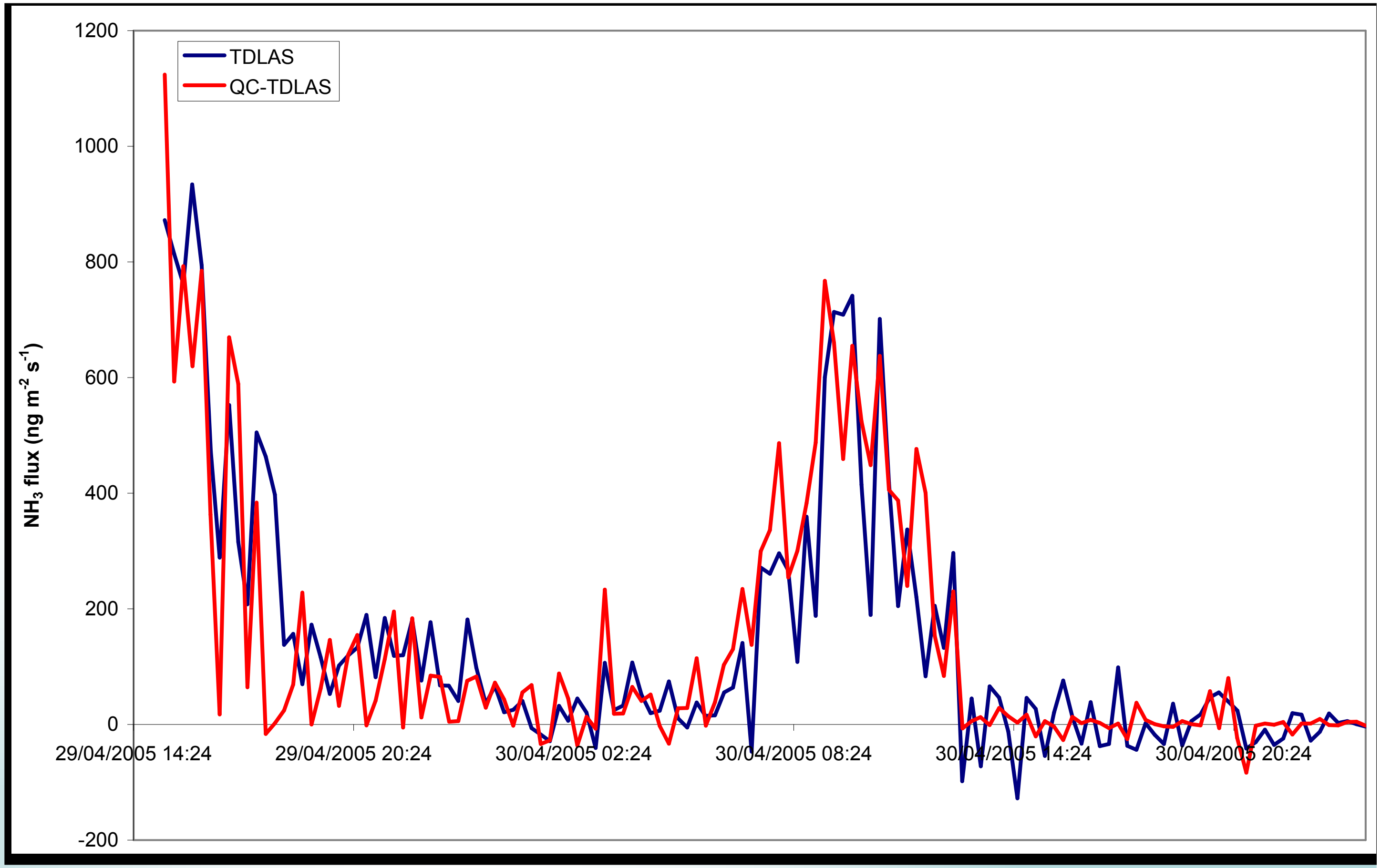

Eddy covariance for NH_3 now possible
– but still not easy

See poster(s) by Jamie Whitehead & Marsailidh Twigg

Terrestrial sinks for PAN may be significantly underestimated

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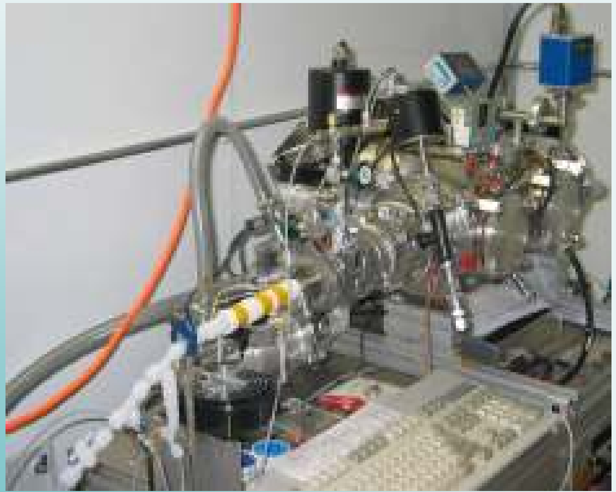
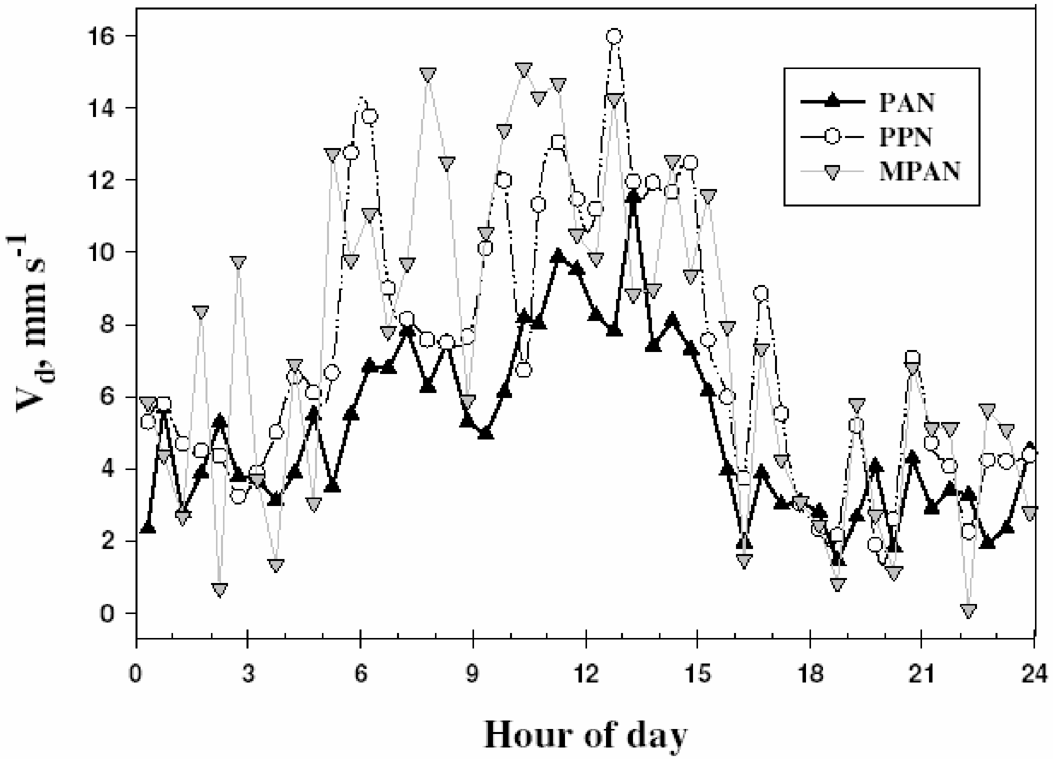
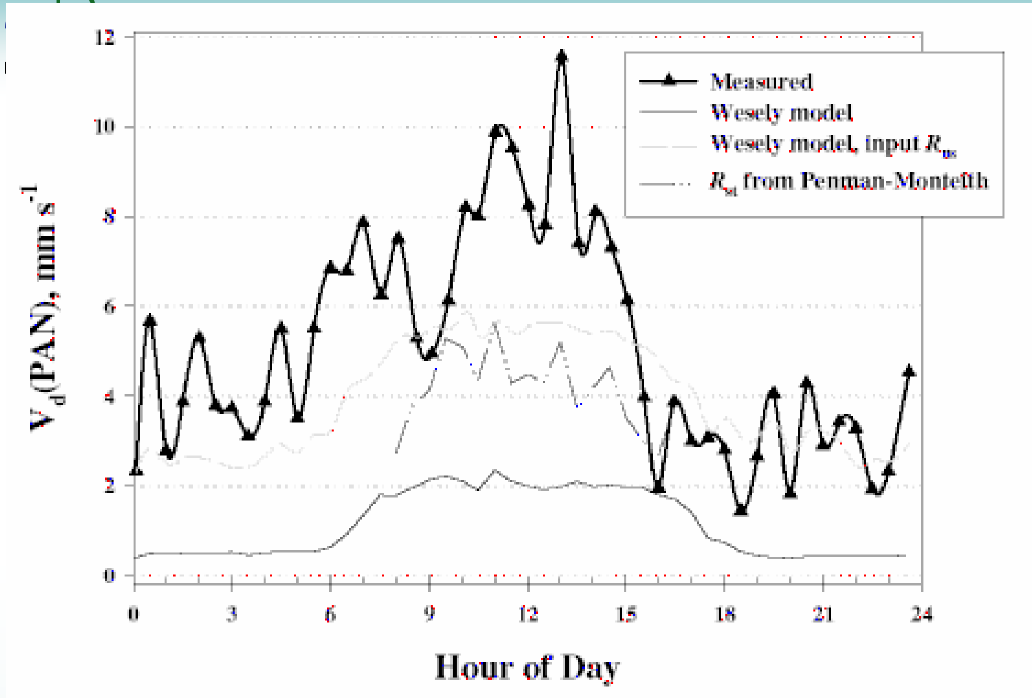
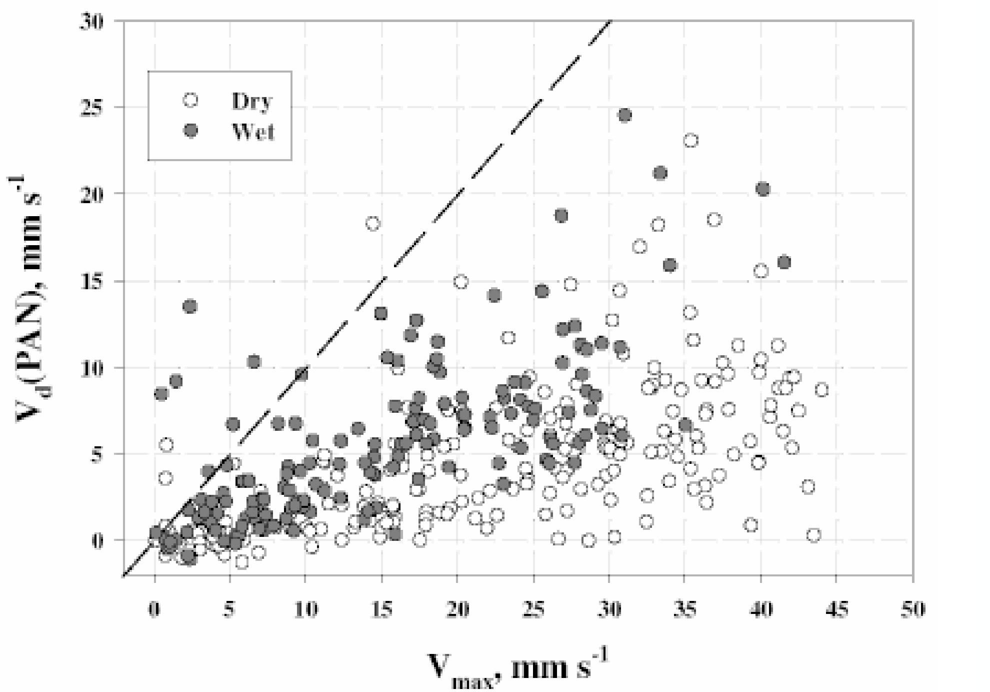


Eddy-covariance measurements of (speciated) PAN fluxes above vegetation at Duke Forest, North Carolina.



Turnipseed, Nemitz . JGR [in press]





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Results:

- Deposition rate about 5 times larger than current model predictions (Wesely).
- Deposition to wet canopies exceeds deposition to dry canopies.

Questions regarding processes:

- What processes enhance the deposition rate of PAN, especially to wet surfaces?
- Are the results transferable to other plant canopies?
- Implications for uptake by cloud?
- Is there a difference between interactions with leaf surface water and sea water? – Probably!

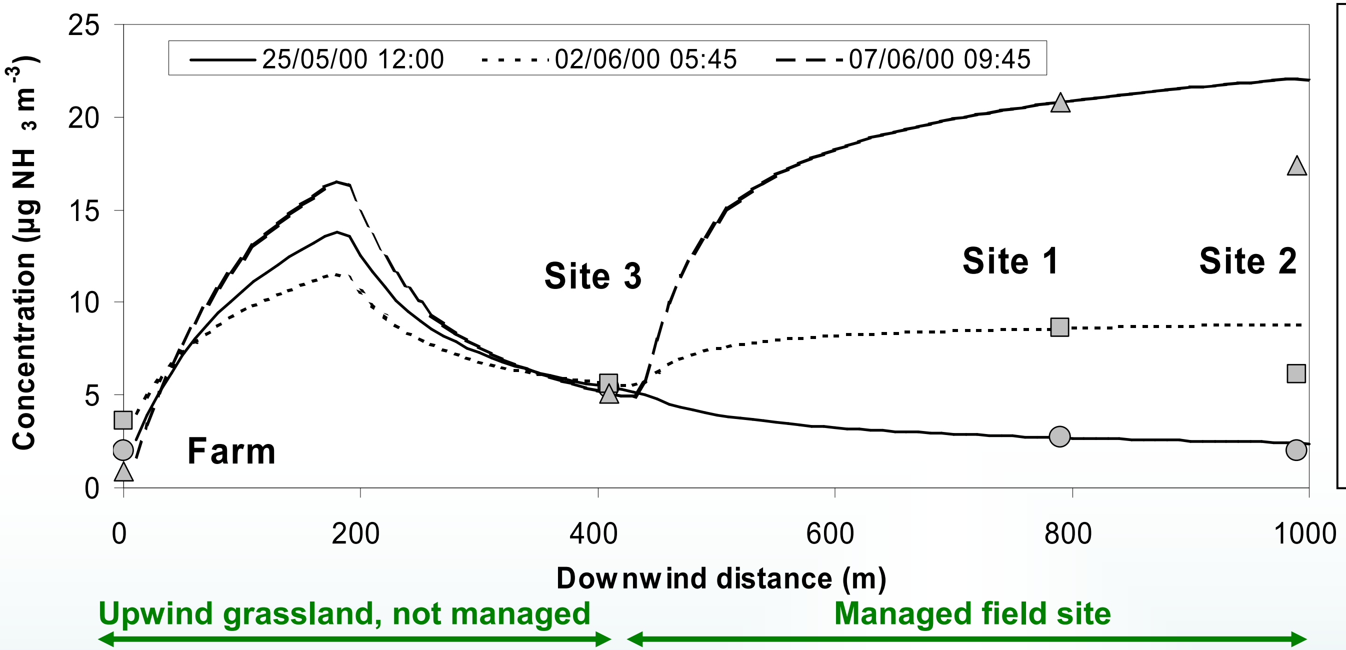
Questions regarding implications:

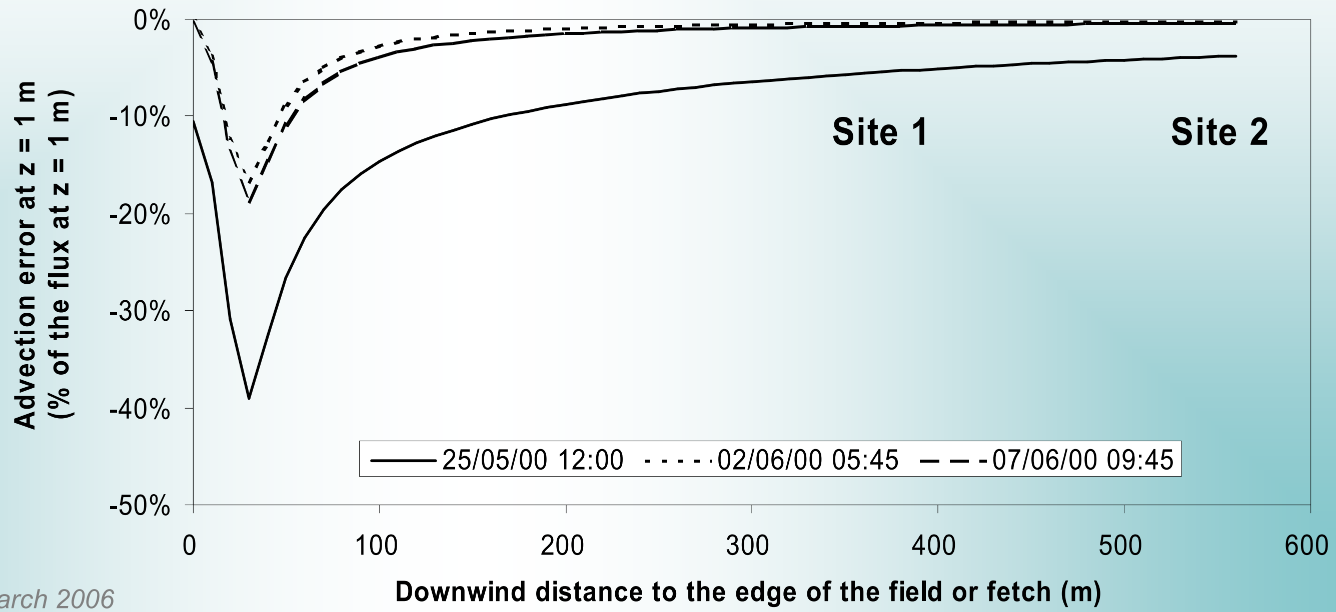
- What are the implications for long-range transport of NO_y to remote regions?
- Terrestrial sinks larger → sources larger (e.g. isoprene emissions)

Improved Theoretical Concepts

- Theory of long-term averaging flux measurement approaches
- Harmonised approaches to estimate fluxes of N_r compounds and non-CO_2 (e.g. filtering, gap-filling etc.)
- Tools to derive fluxes in conditions of vertical flux divergence: theory development and validation measurements
  - Chemical interactions (NH_3-HNO_3-NH_4NO_3; NO-NO_2-O_3)
  - Advection errors due to local ground-level sources (particularly of NH_3)

Quantification of advection errors during GRAMINAE experiment





Loubet *et al*. (in prep.)

Summary I

- **NitroEurope will require measurement technologies at three levels of complexity**
- **Level-1 methodology for concentration measurements is established**
  - DELTA samplers being distributed to about 50 sites
  - Four central analytical facilities being established
- **Low-cost flux methodology will be developed**
  - To expand flux network (Level-2 sites)
  - To add NH_3/HNO_3/NH_4^+/NO_3^- flux measurements to Level-3 sites
  - As the basis for a potential network expansion beyond the time frame of NitroEurope

Summary II

- NitroEurope does not have the funds to purchase major state-of-the-art equipment (AMS, CIMS, TDL-AS, GRAEGOR)
- Targeted resources are allocated to
  – Further develop existing instrumentation
  – Apply instrumentation at Level-3 sites in 'Special Topic' studies
    - to quantify selected component fluxes of particular importance at individual sites
    - to study processes controlling fluxes of N compounds that are difficult to measure (HNO_3, NH_4^+, NO_3^-, organic N)
  – Develop improved analysis methodologies (e.g. to deal with vertical flux divergence)

Acknowledgements

- **CEH colleagues** (Mark Sutton, Sim Tang, Celia Milford, Marsailidh Twigg, Chiara di Marco, Ute Skiba, Rick Thomas, Gavin Phillips, Ron Smith, Stephanie Jones)
- **EXAMINE & GRAMINAE communities** (Benjamin Loubet, Arjan Hensen, Jan Willem Erisman, Rene Otjes, Piet Jongejan, Martin Gallagher, Mike Flynn, Jamie Whitehead, Laszlo Horvarth, Ulrich Daemmgen, Albrecht Neftel)
- **US colleagues** (Andrew Turnipseed, Greg Huey)
- …