Ammonia / ammonium interactions:

Effects on surface/atmosphere exchange fluxes and the atmospheric aerosol loading

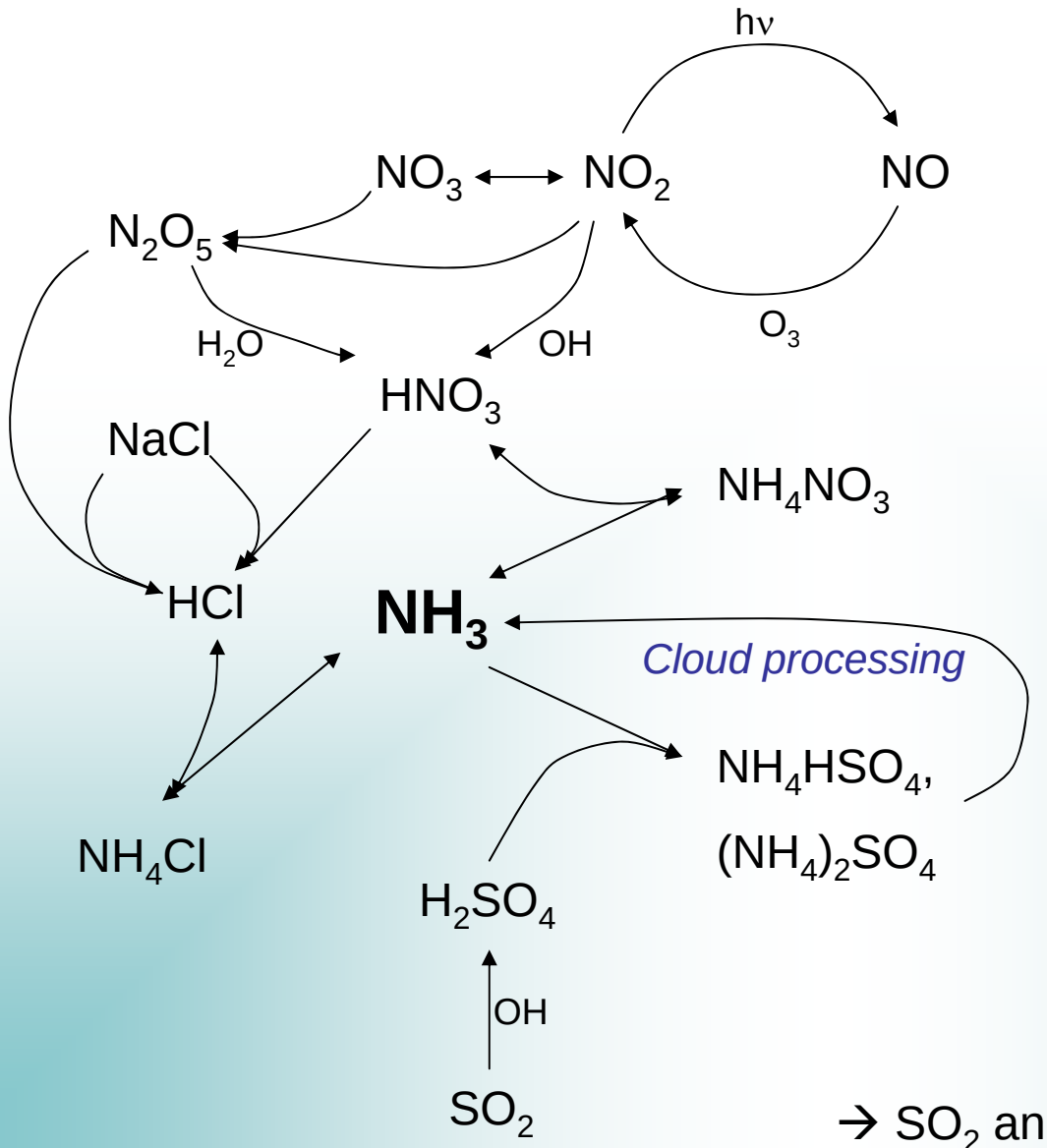
Eiko Nemitz, Gavin Phillips, Rick Thomas, Mark Sutton, Marsailidh Twigg, Daniela Famulari, Sim Tang, Ron Smith, David Fowler:

Centre for Ecology and Hydrology (CEH) Edinburgh, U.K.

Ammonia Chemistry

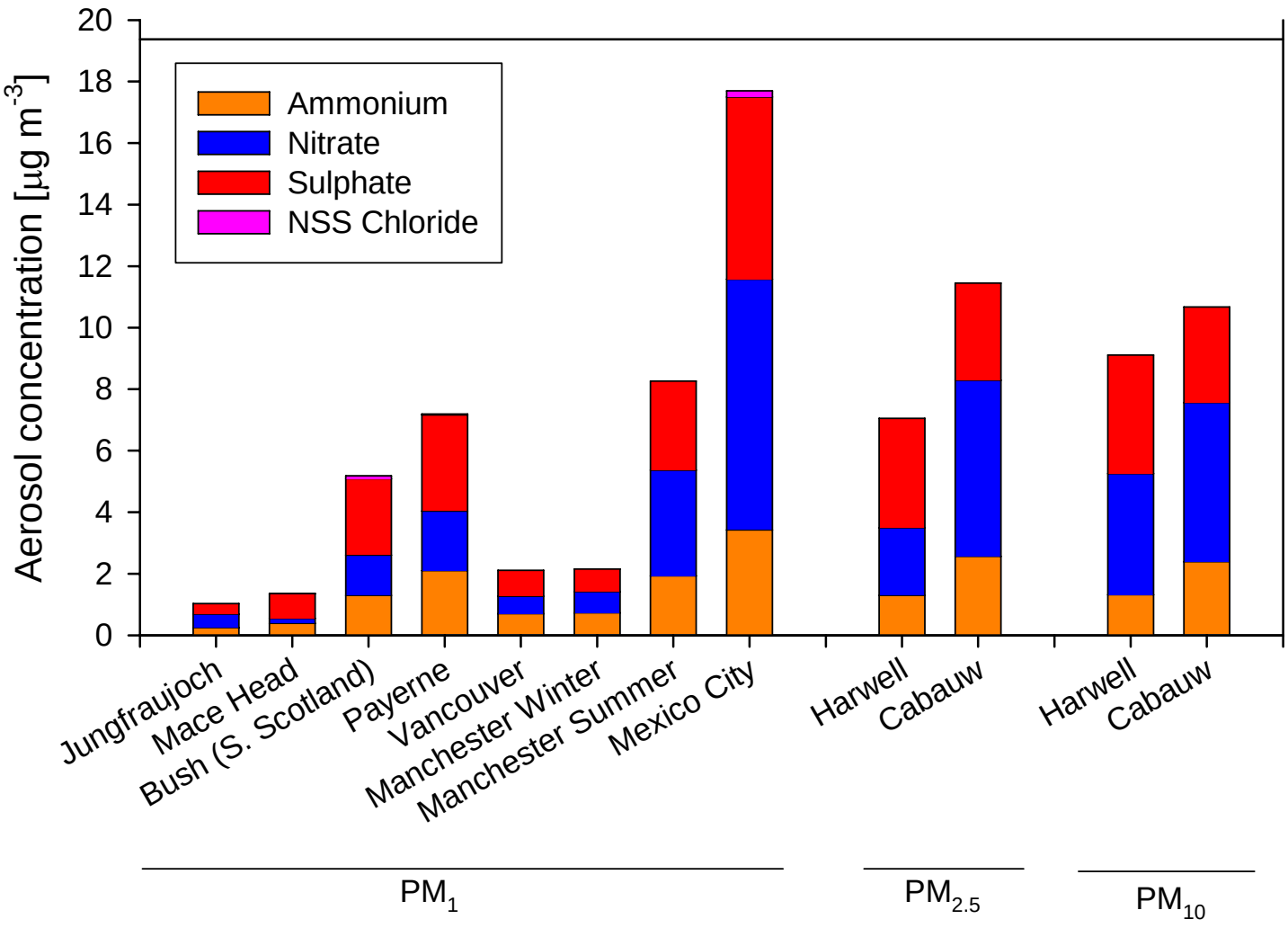
1. Ammonia as an aerosol precursor
   - Contributing to PM with impacts on human health
   - Radiative cooling
   - Promoting nucleation
2. Processes controlling gas-to-particle conversion
3. Effects of chemistry on the measurement of surface / atmosphere exchange fluxes (NH_3, aerosols, acids)

Ammonia as an Aerosol Precursor

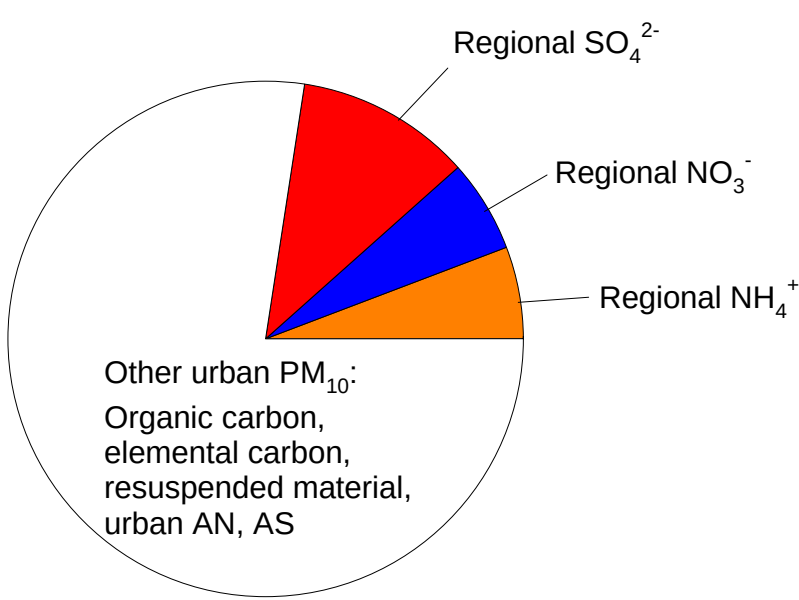


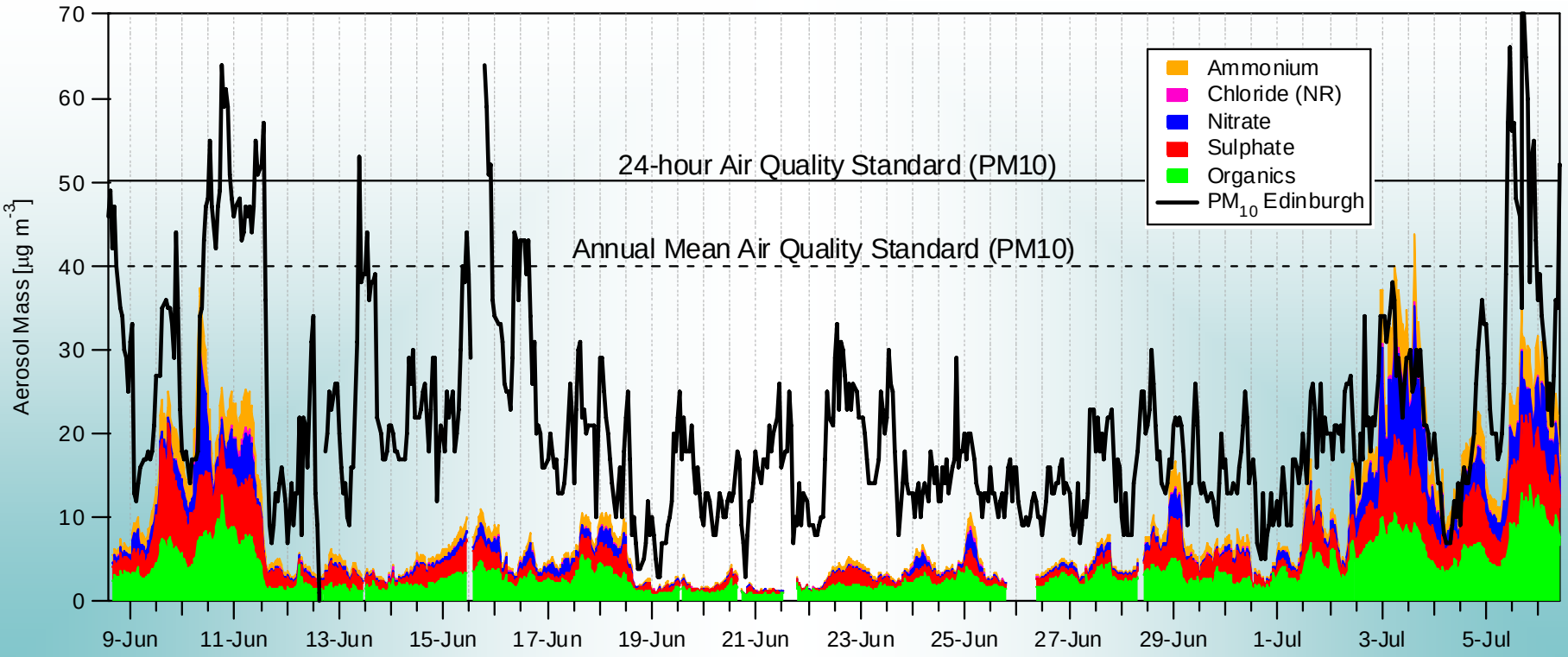
→ SO_2 and HNO_3 compete for the NH_3

Concentrations of Ammonium Aerosols

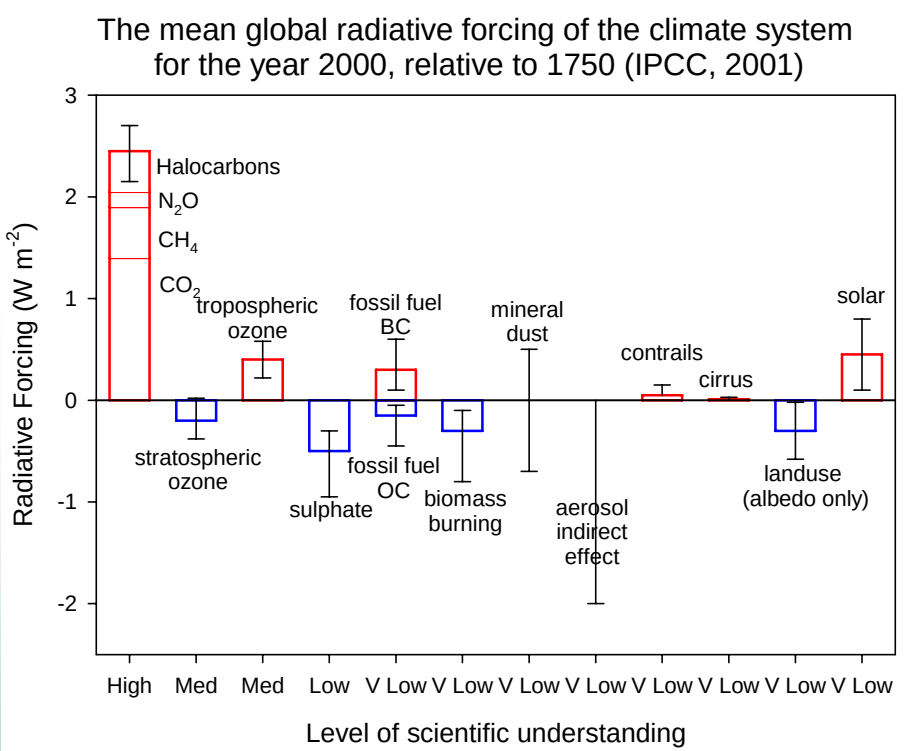


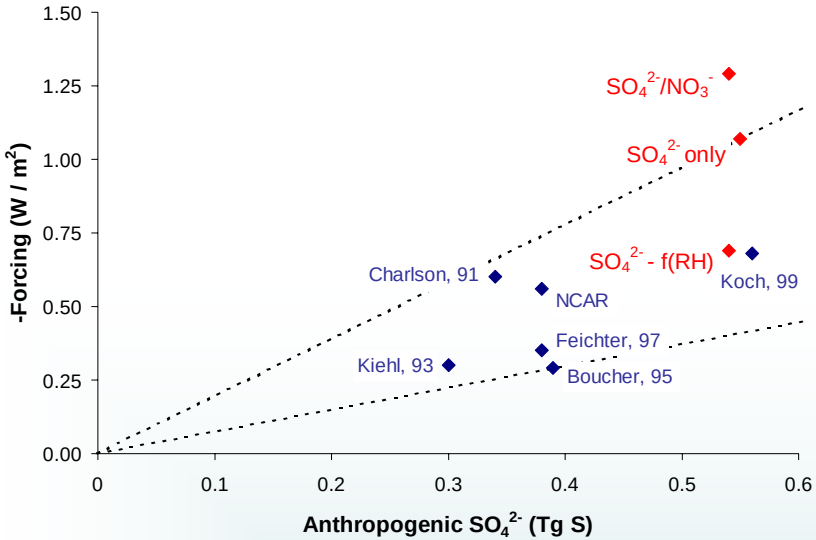
Contribution of Regional Ammonium Aerosols to Exceedances of PM_{10} Air Quality Standards in Urban Areas

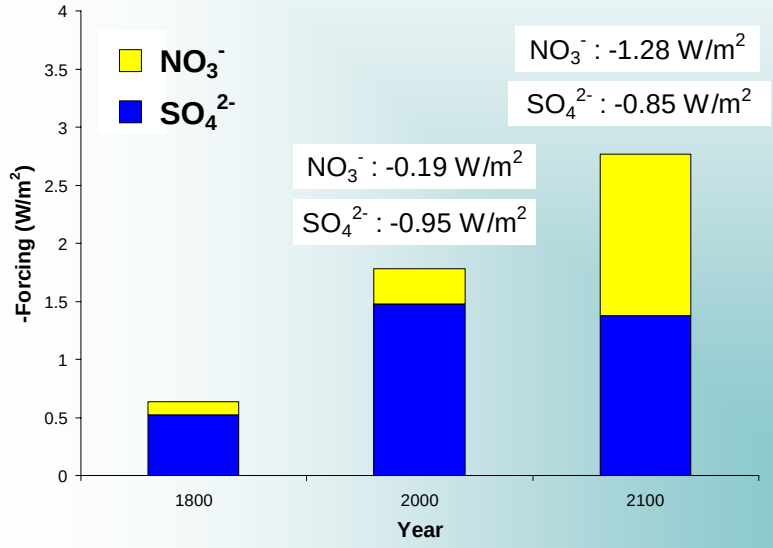




Climate Forcing of Ammonium Aerosols

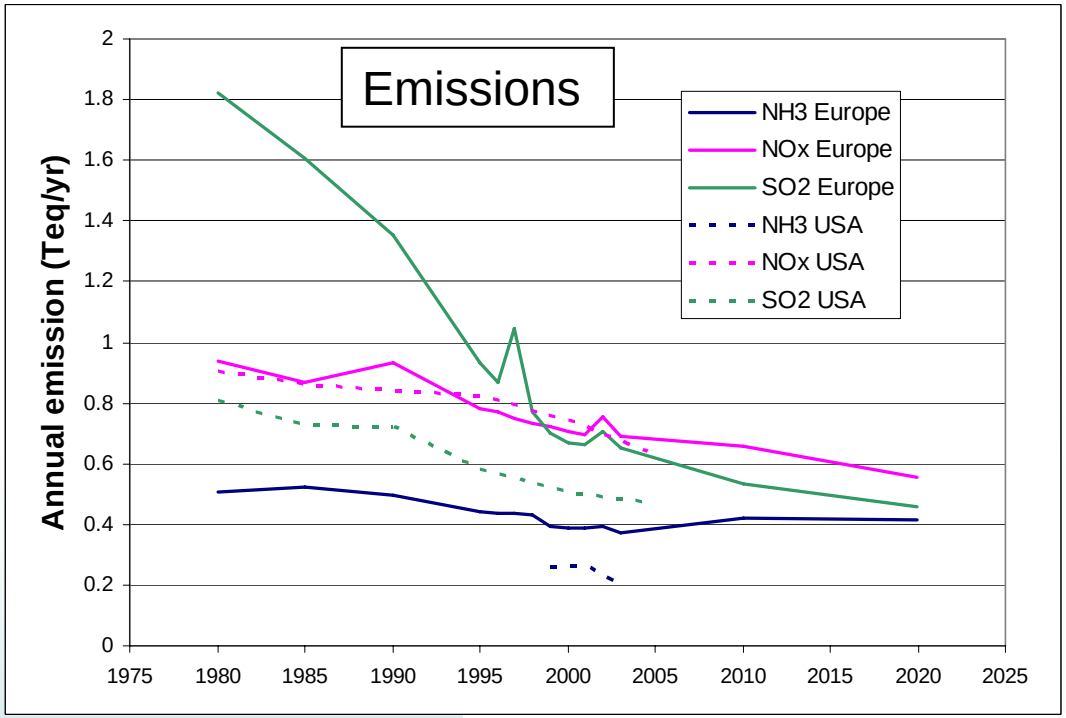




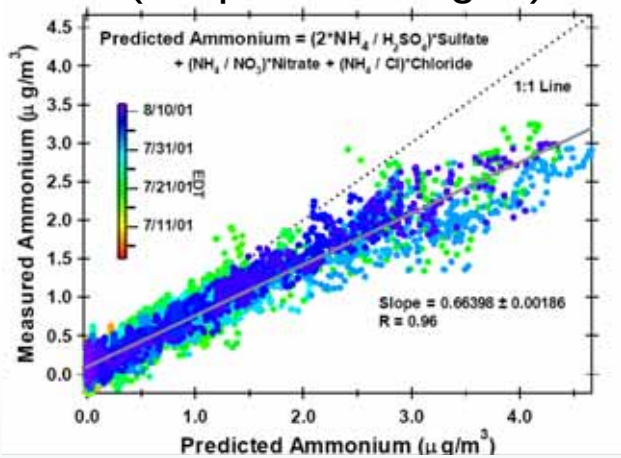


Adams, Seinfeld et al., *J. Geophys. Res.*, 106, 1097-1111, 2001

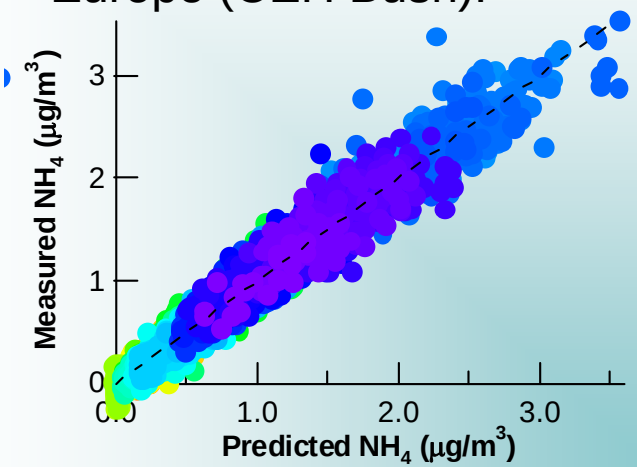
European vs. US Aerosol



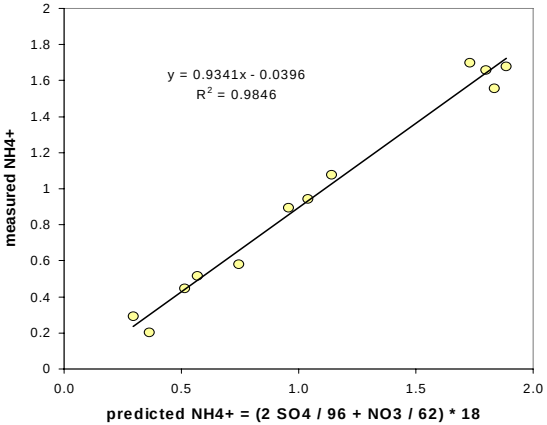
USA (Prophet, Michigan):



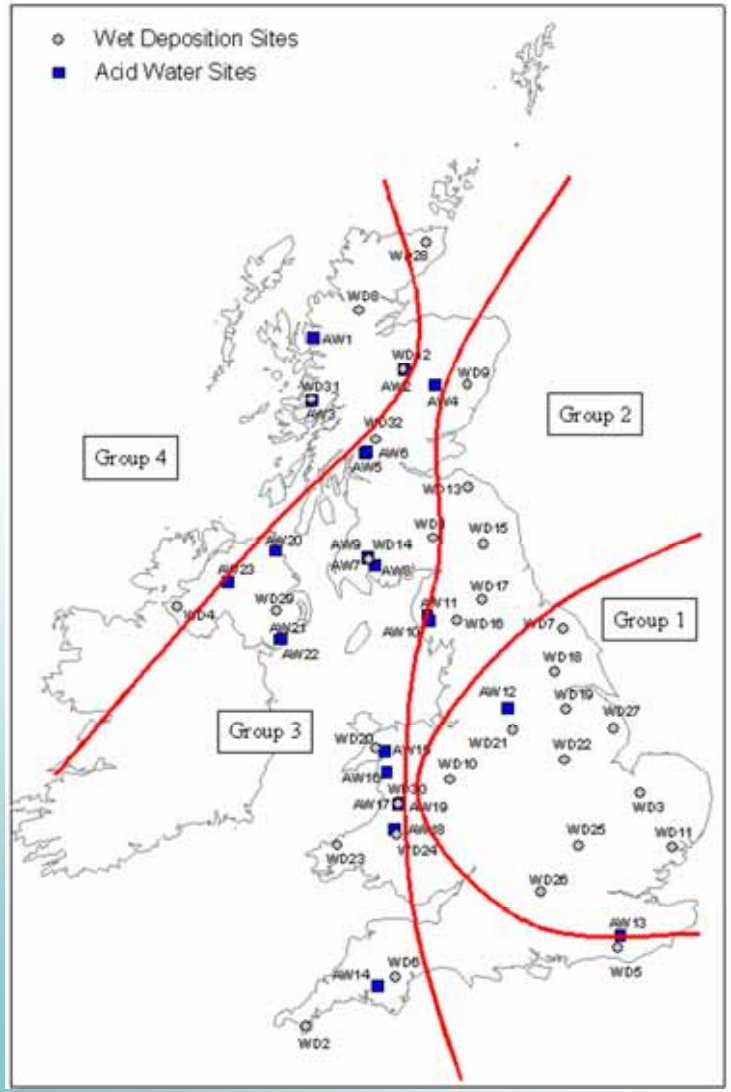
Europe (CEH Bush):

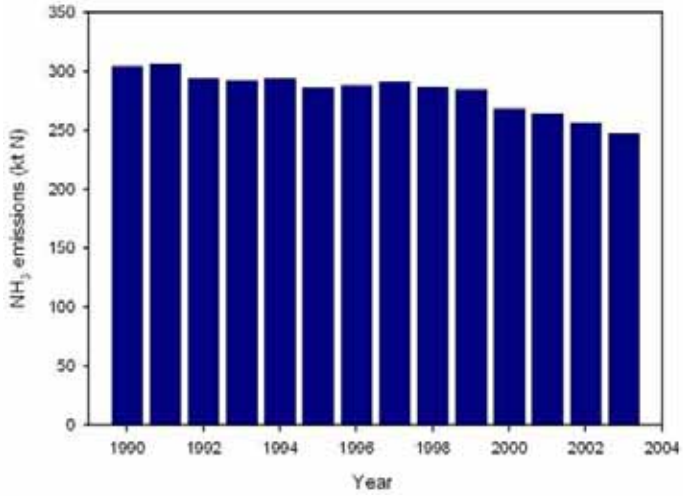


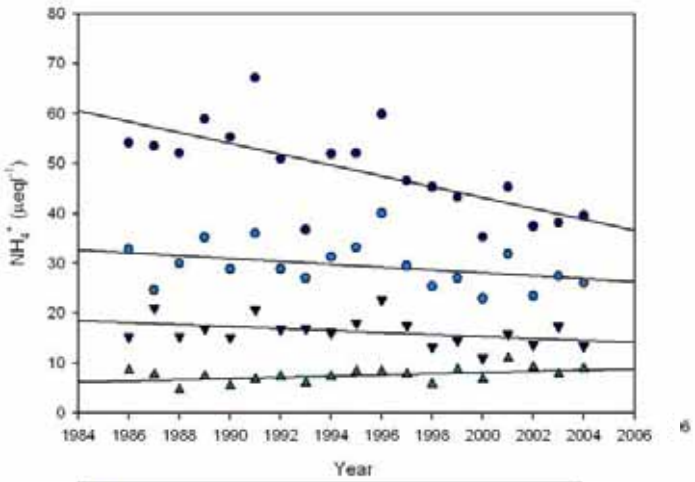
UK network:



Shift from $(NH_4)_2SO_4$ to NH_4NO_3 Chemistry



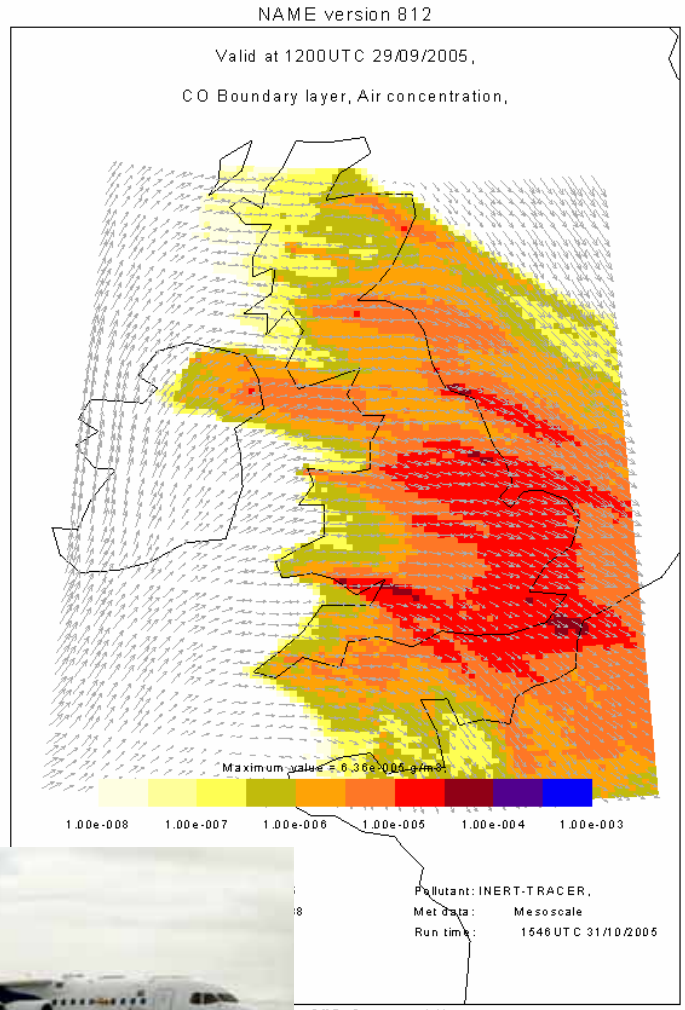


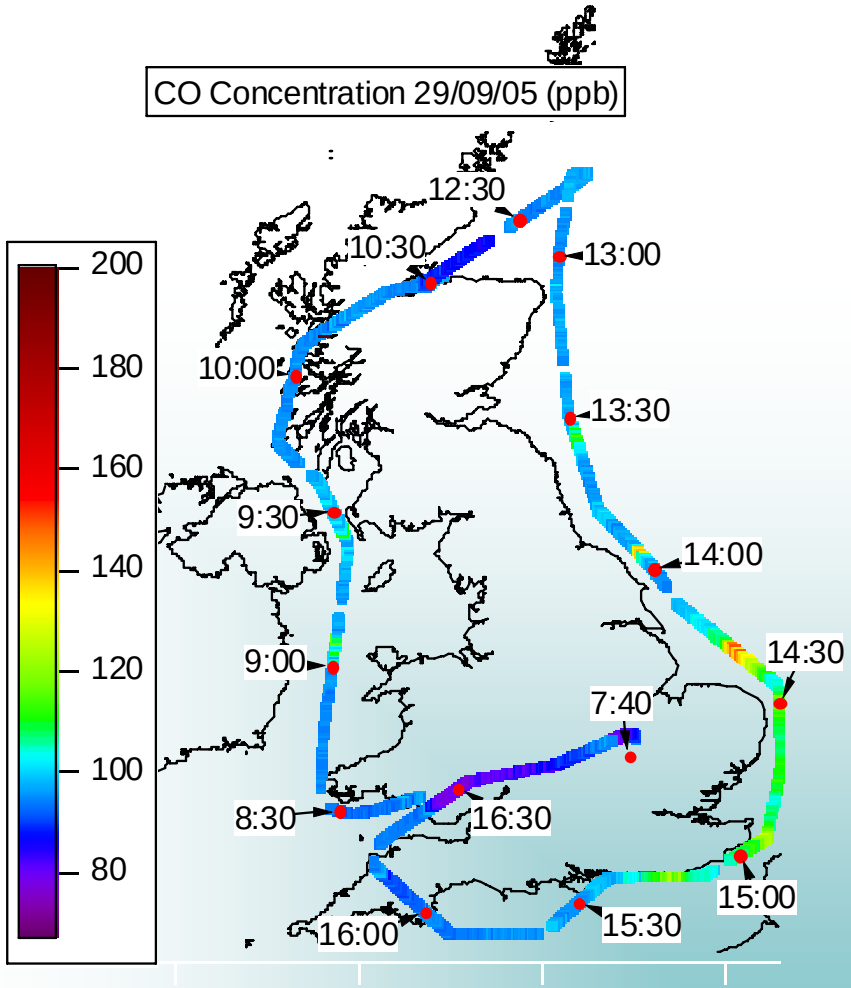


Modelling the Response of Ammonium Concentration to Emission Reduction of Precursor Gases

- S. German study (S. Drechsler *et al.,* 2006):
  - In the rural environment AN formation is NH_3 limited and responds to changes of NH_3 only.
  - In the urban environment AN formation is NO_x limited and responds to changes of NO_x only.
- Swiss study (Spirig and Neftel, 2006):
  - 10% reduction of NH_3 emissions → 0.5% decrease in PM_{10}
  - 50% reduction of NH_3 emissions → 3-10% decrease in PM_{10}
- Easter US winter study (Vayenas et al., JGR, 2005):
  - Sulphur reduction by 50% → inorg. $PM_{2.5}$ reduction of 8-23%
  - Ammonia reduction by 50% → inorg. $PM_{2.5}$ reduction of 29%
  - Nitric acid reduction by 50% → inorg. $PM_{2.5}$ reduction of 17%

Time-scales of NH_4NO_3 Formation





NO_2-NO_3^- oxidation rate (B111-14/07/05)

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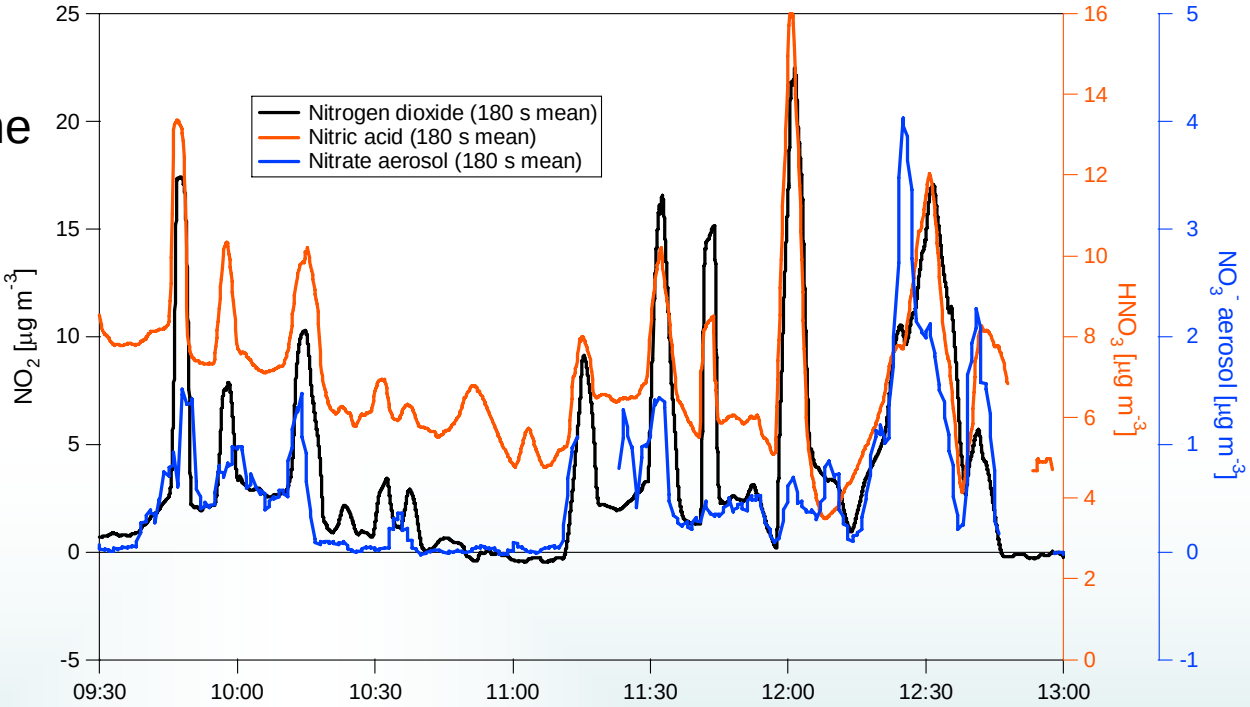
10:15 – Central Scotland plume
11:35 – Newcastle plume
12:00 – Midlands plume
12:30 – London plume



Average wind speed = 4.48m/s
Average wind direction = 208deg

	10:15	**11:35**	**12:00**	**12:30**
Distance aircraft from source (km)	90	50	70	100
Air parcel travel time (hours)	5.6	3.1	4.3	6.2
% N oxidised to HNO_3 (%)	22.8	20.3	32.5	35.5
% N oxidised to NO_3^- (%)	9.4	7.5	2.1	16.6
Oxidation rate to HNO_3 (%N hr^{-1})	4.1	6.6	7.5	5.7
Oxidation rate to NO_3^- (%N hr^{-1})	1.7	2.4	(0.48)	2.7
Total oxidation rate (%N hr^{-1})	5.8	9.0	8.0	8.4

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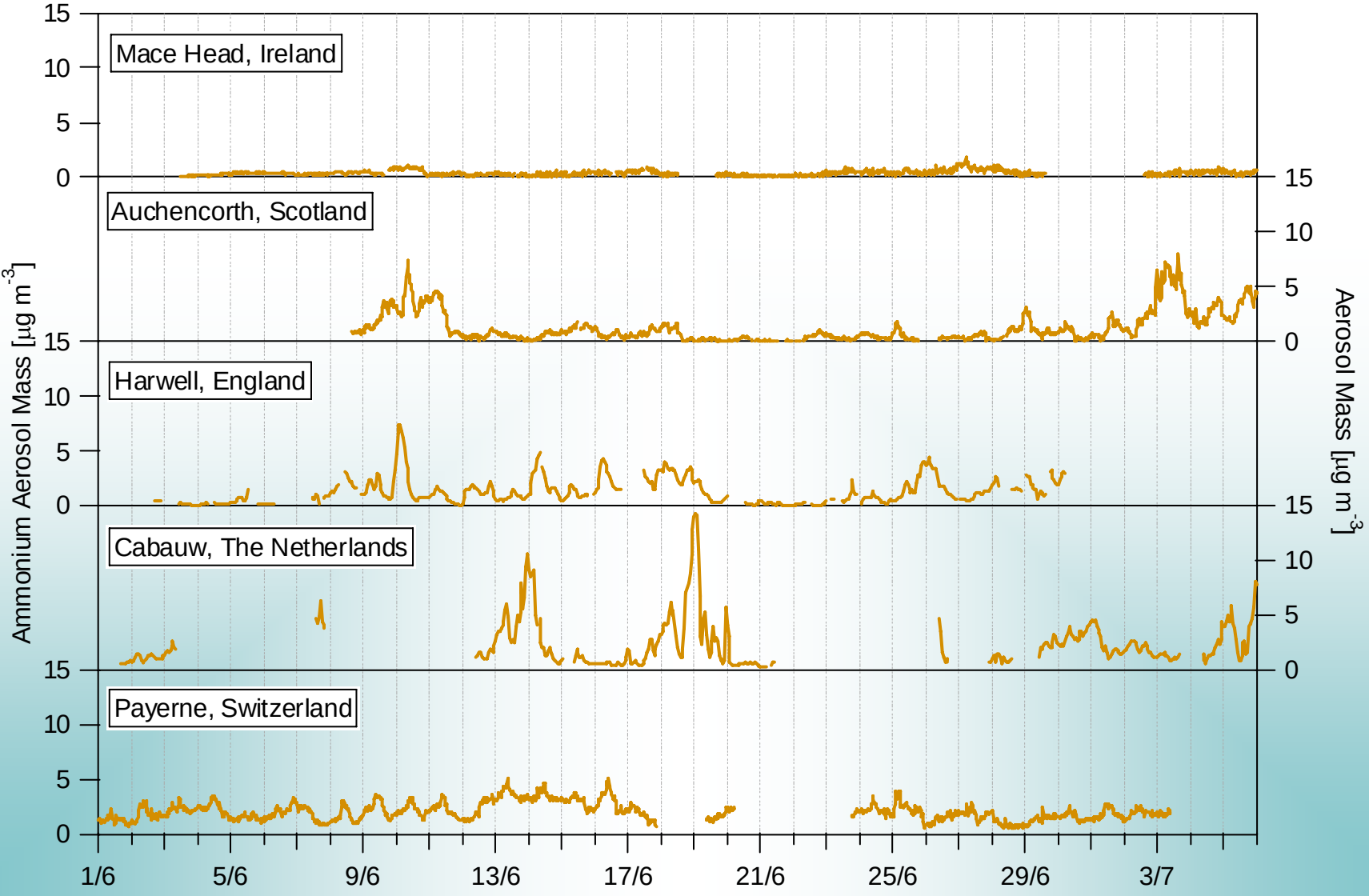
Highly resolved Ammonium measurements across Europe

(1st EMEP Intensive Measurement Period, June 2006; unratified)



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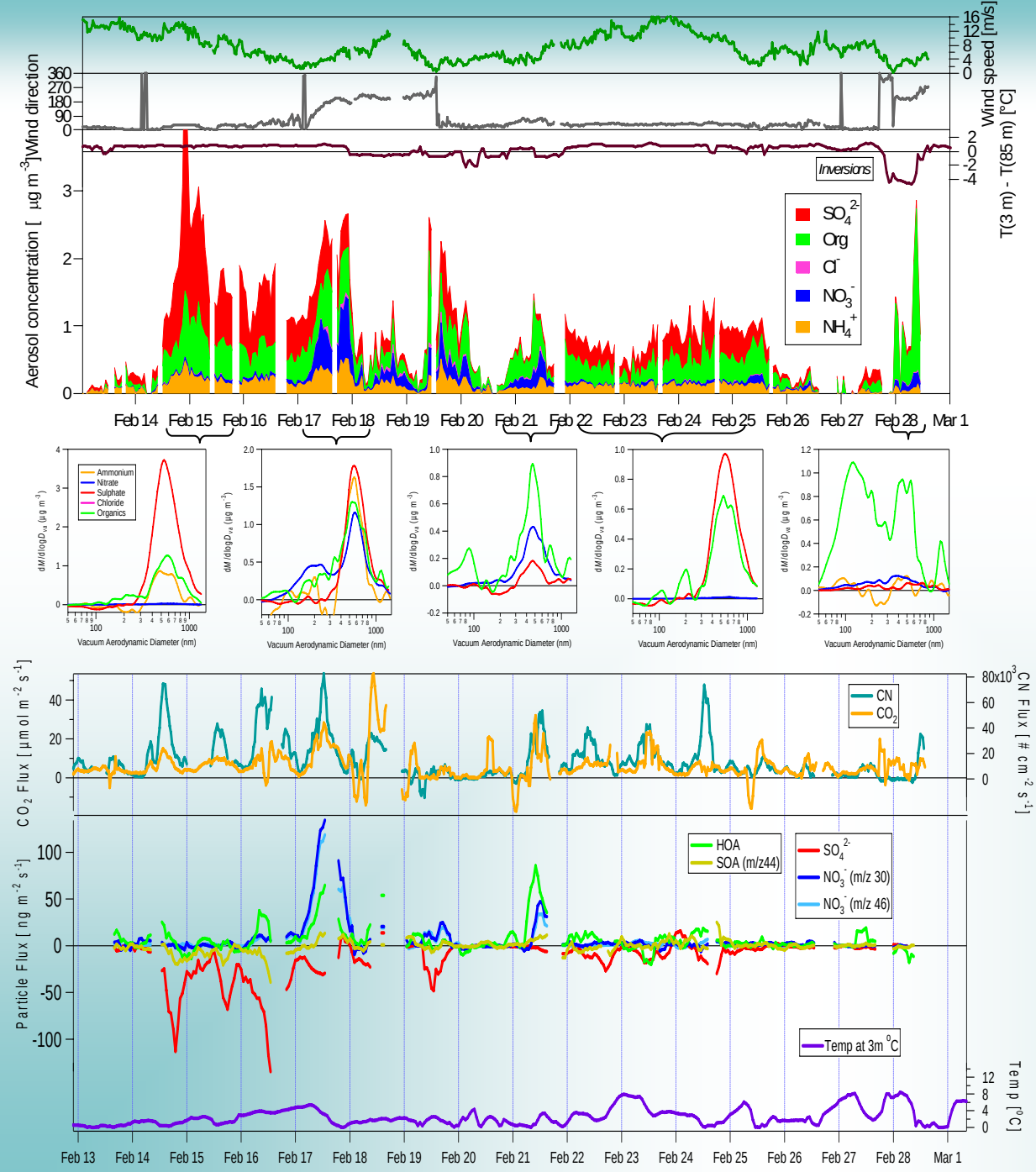
Urban Aerosol Fluxes by Aerosol Mass Spectrometry (Gothenburg)



Results:

- Aerosol nitrate emissions from urban areas appear to be ubiquitous, indicating that NO_x oxidation is very fast.
- Nitrate formed in urban areas is in the Aitken mode (observed worldwide).
- They occur during both summer and winter, but vary between days.
- In winter emissions appear to be larger on inversion days (build-up of HNO_3 & NH_3?)

Observations of Aerosol Nitrate Fluxes above Urban Areas

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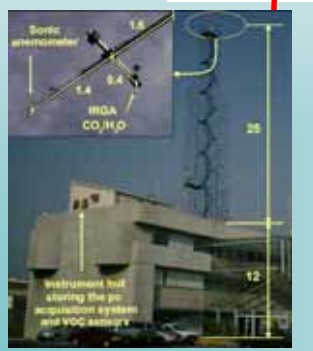
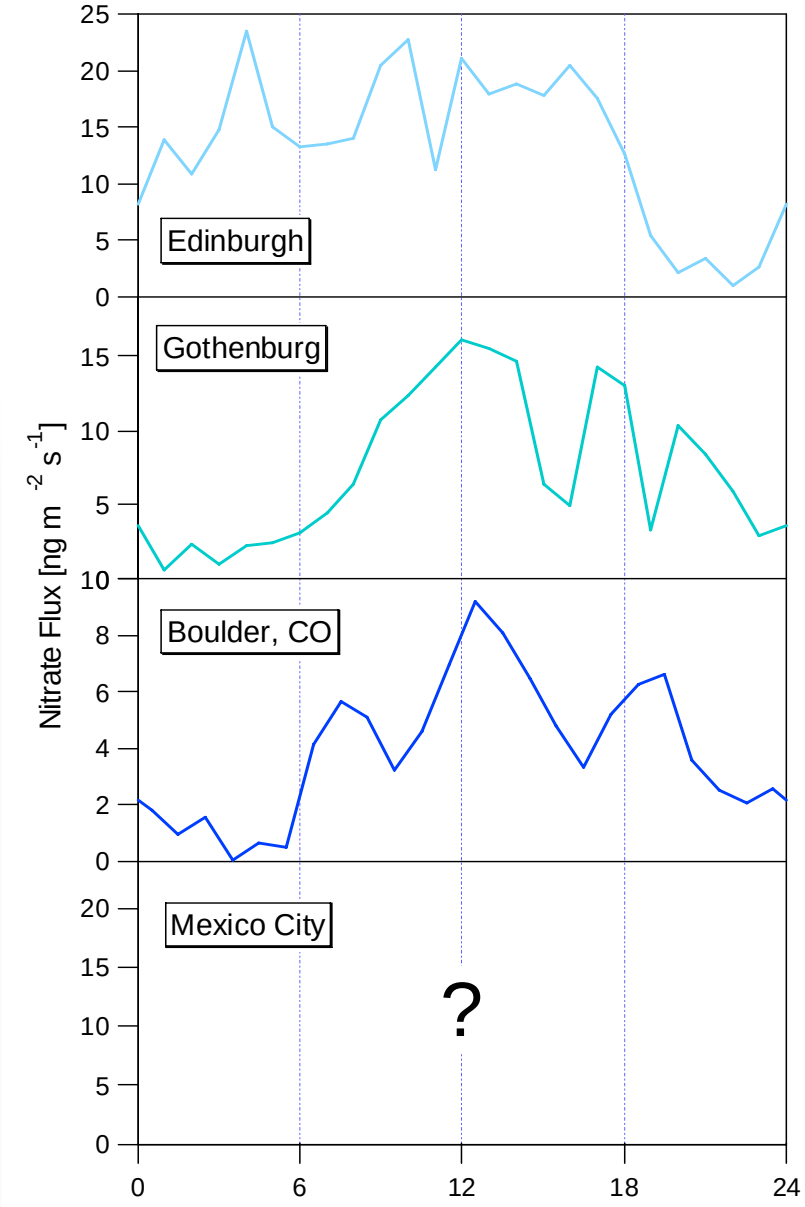
Boulder, CO
(80,000)

Gothenburg
(480,000)



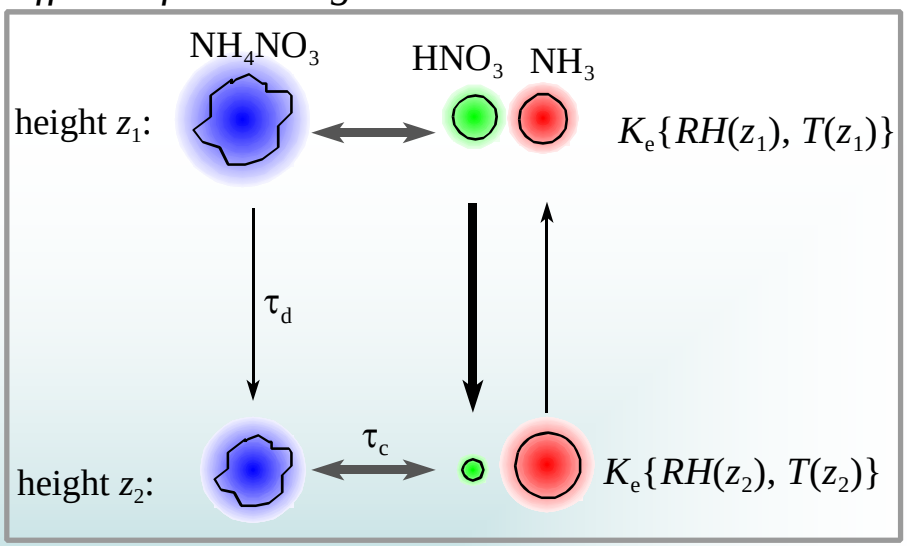
Mexico City
(20,000,000)

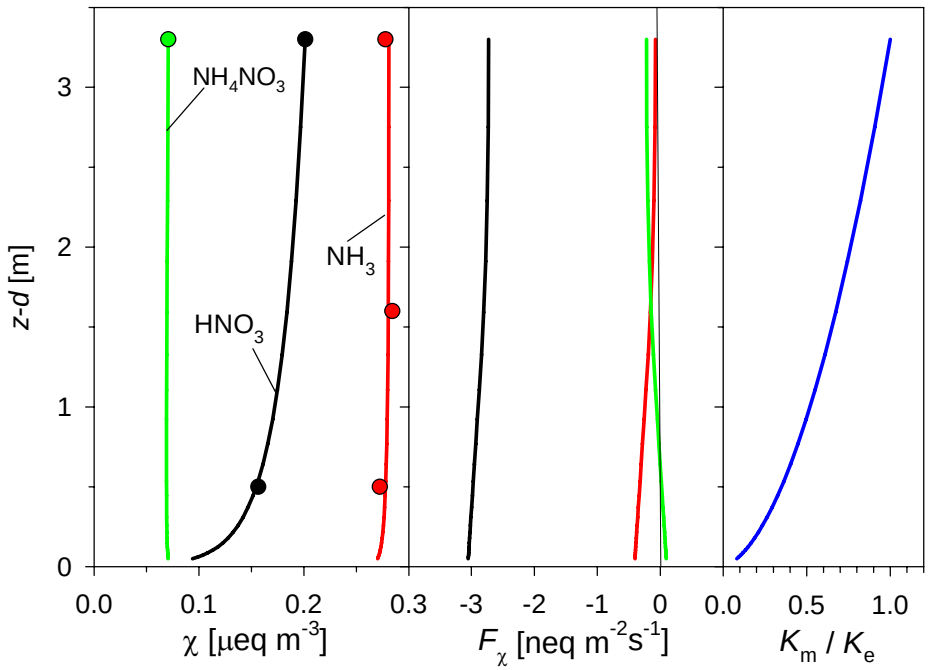
Edinburgh
(435,000)



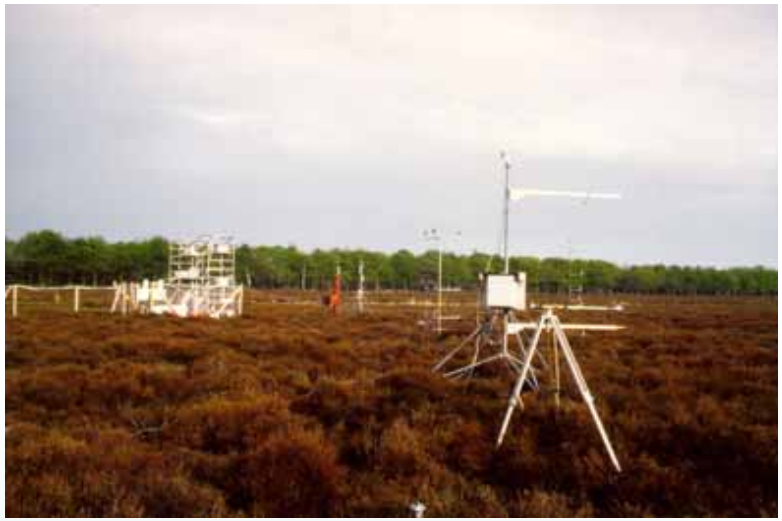
Effects of Chemistry on Flux Measurements

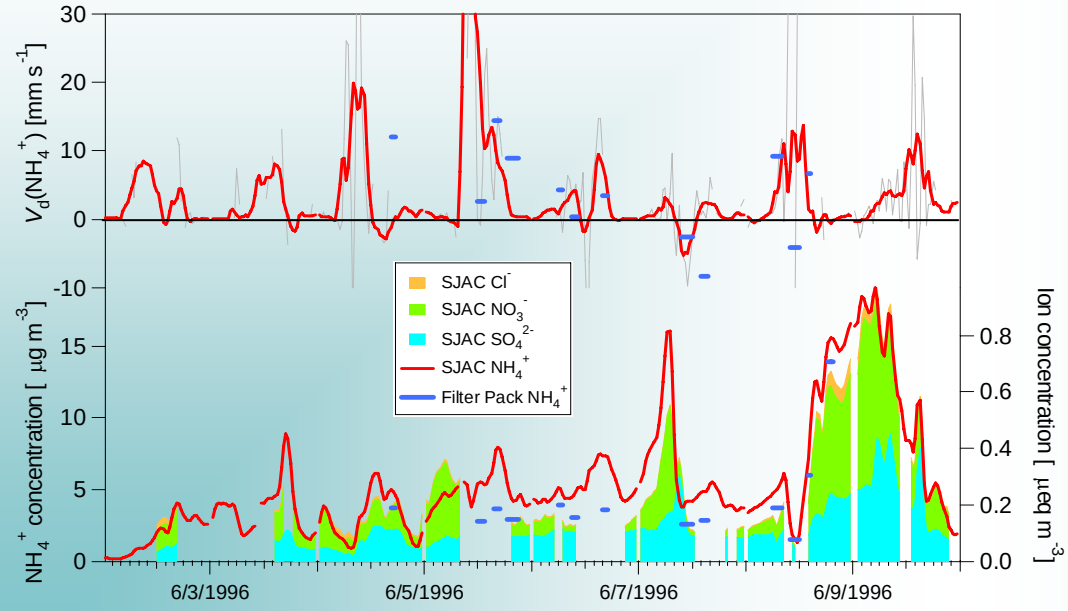
Effects of vertical gradients.

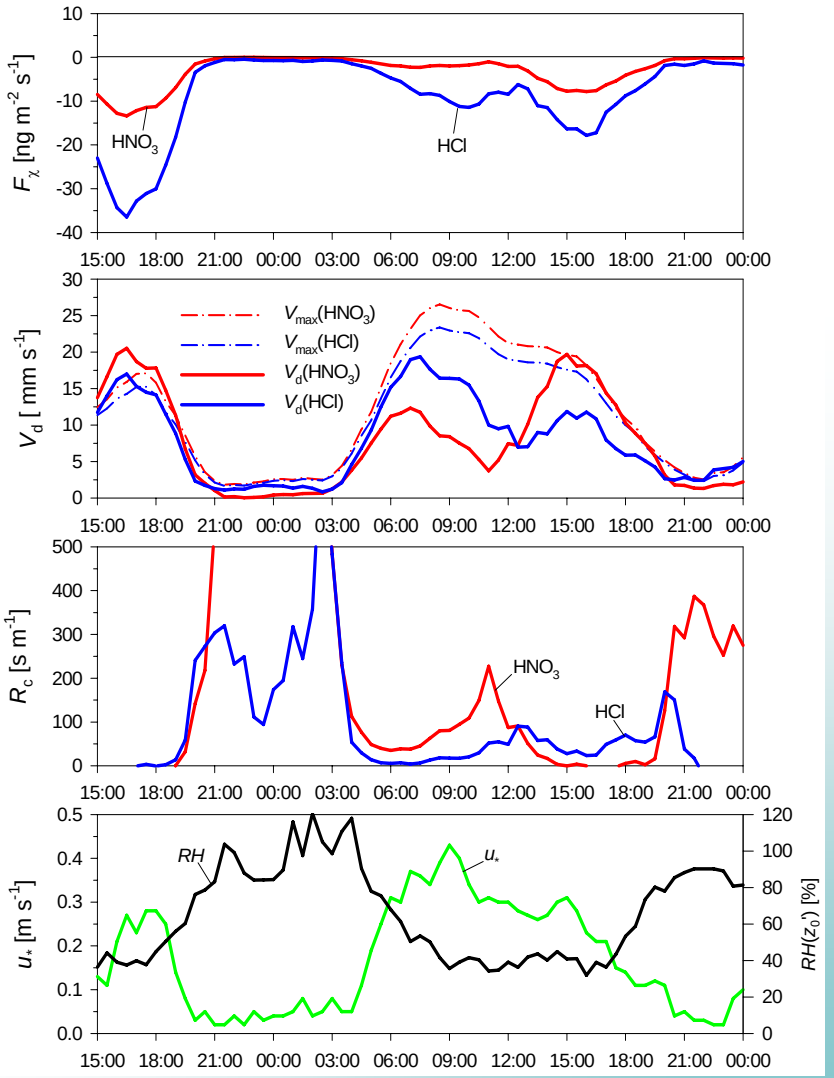




Example 1:
NH_4NO_3 evaporation above heathland

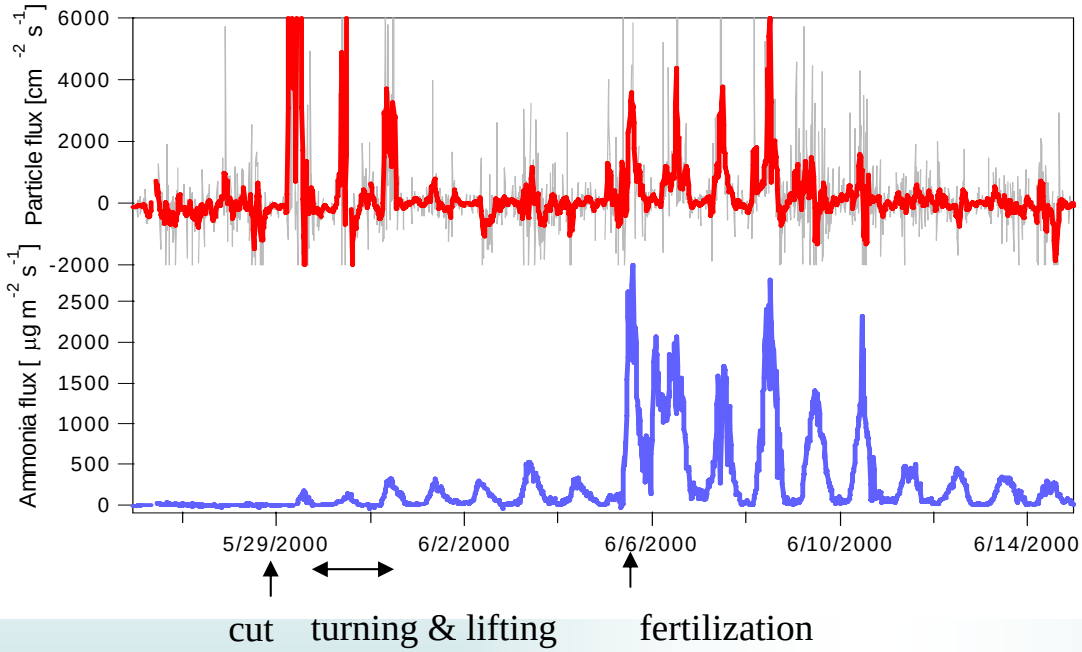


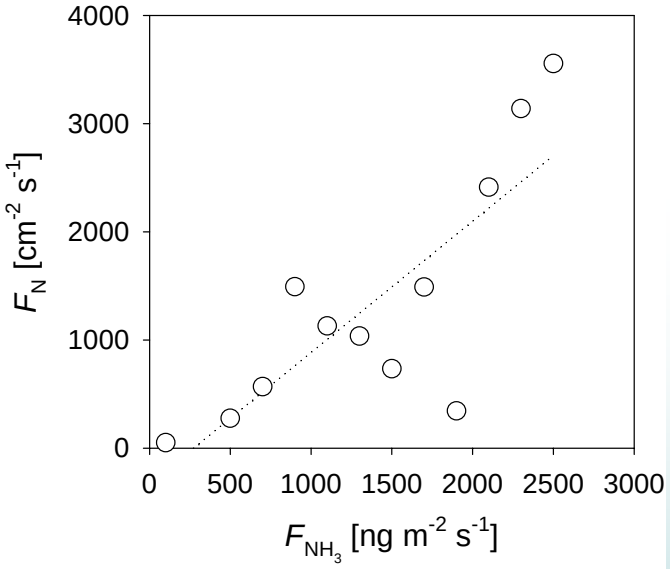


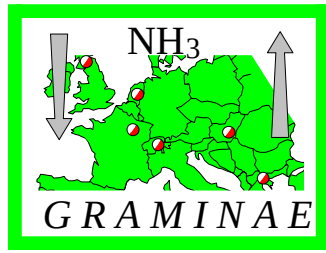


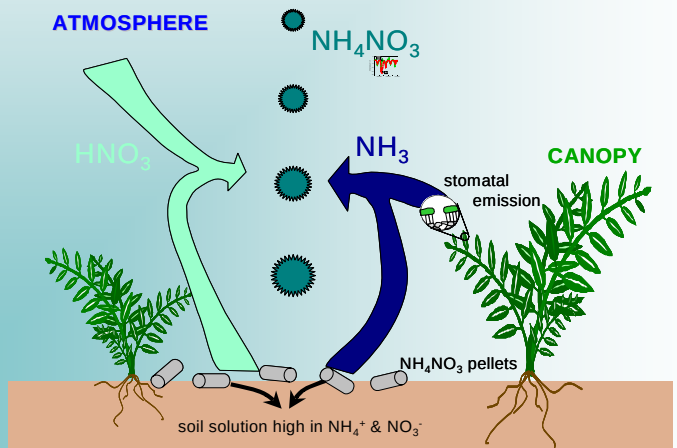
Example 2:

Aerosol growth above a NH_4NO_3-fertilised grassland









1) At about 400 to 450 nm hr^{-1}, growth rates of 11 nm particles are fast. In this NH_3-rich environment 200 nm particles grow at 40 to 45 nm hr^{-1}, an order of magnitude faster than after nucleation bursts in semi-natural environments.

2) Average NH_4NO_3 production rates are 52 and 78 µg m^{-3} hr^{-1} during the day and at night, respectively.

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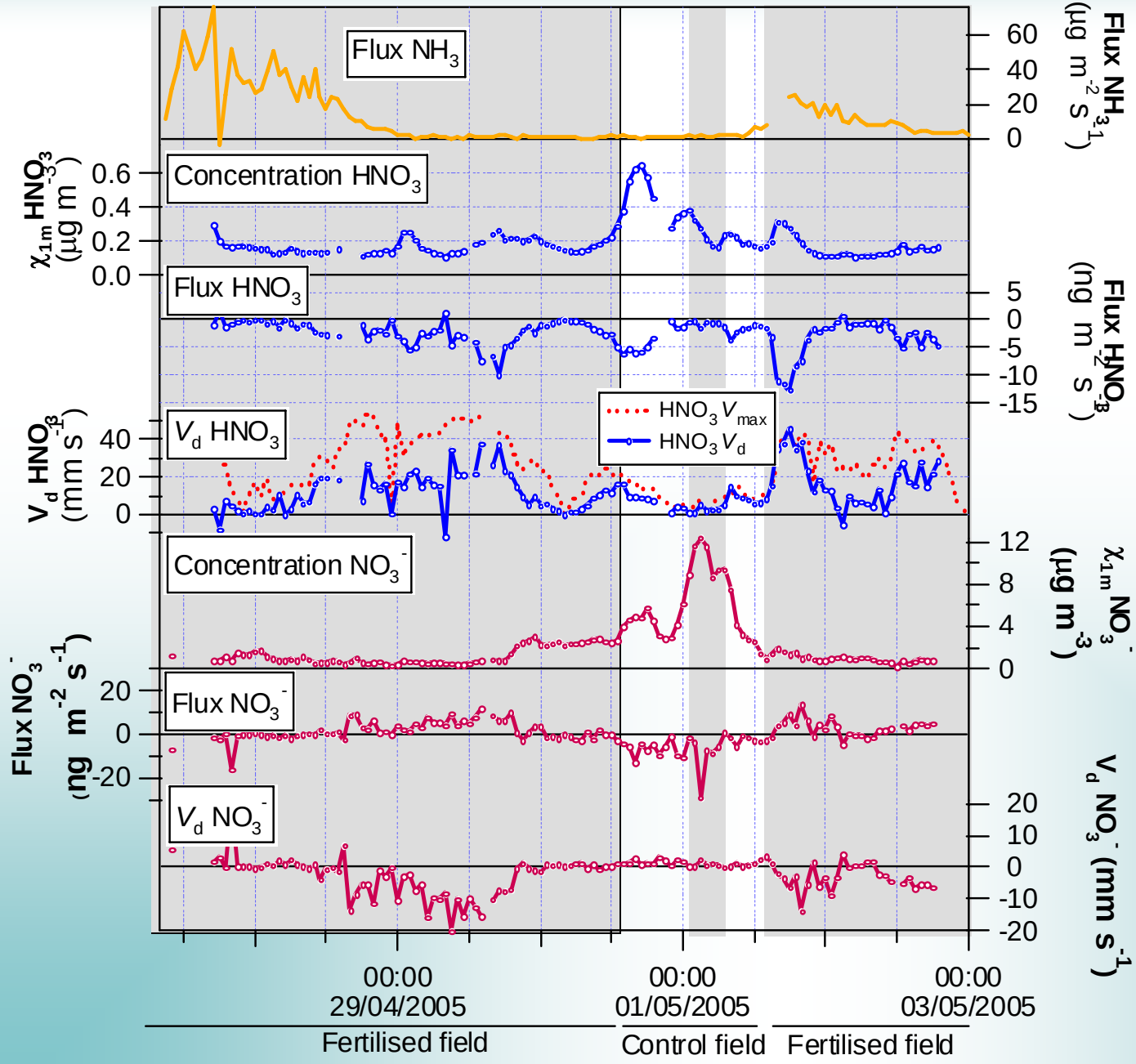
Example 3:
Aerosol formation following slurry application



Summary I: Ammonium Concentrations

- Ammonium aerosols (AN, AS) are ubiquitous in the atmosphere; contribution from AC is usually negligible
- Regional AN & AS make an important contribution to exceedances of Air Quality Standards in urban areas
- The cooling of ammonium aerosols is thought to be - 0.5 (- 0.25 to – 1.2) W m^{-2}
- European aerosol is generally neutralised; US aerosol is often acidic.

Summary II: Changes in Ammonium

- There is an ongoing shift from sulphates to nitrates, complicating the description of the chemistry.
- Responses to reduction in precursor gases are poorly understood and verified.
- The urban environment appears to be an important (under-studied) area of AN production
- Aircraft measurements and EMEP Intensive Measurement Periods provide powerful datasets for model development / validation

Summary III: Effect of Ammonia Chemistry on Fluxes

- Chemistry leads to errors when using standard micrometeorological approaches
- Non-conservation needs to be considered for the interpretation of flux measurements (not just ammonia, but also aerosol)
- The conversion between gas and aerosol phase changes net exchange of NH_x (and also NO_x)
- These processes are confined to the lowest metres of the atmosphere. Larger scale models are not able to reproduce this aerosol formation → need for sub-grid parameterisations.

Acknowledgements

- European funding: EXAMINE, GRAMINAE and NitroEurope IP
- National funding from the UK Department for Environment, Food and Rural Affairs.
- Data sources:
  - Michigan data: Alice Delia, Univ. Colorado
  - EMEP Intensive Campaign:
    - Jan Willem Erisman & Rene Otjes, ECN, NL
    - Univ. Kopio, FI
    - Urs Baltensperger & Rami Alfarra, Paul Scherer Institute, CH

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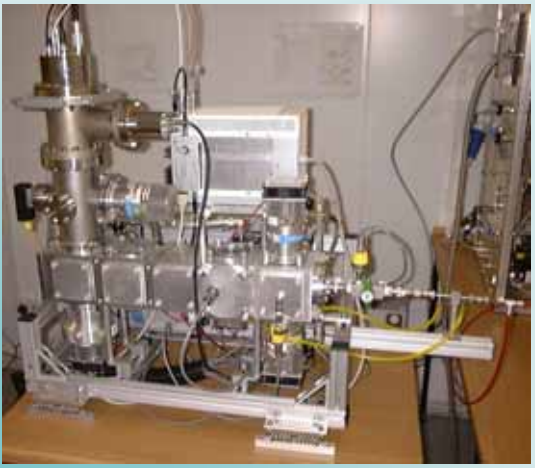
Observations of significant aerosol nitrate formation in urban areas

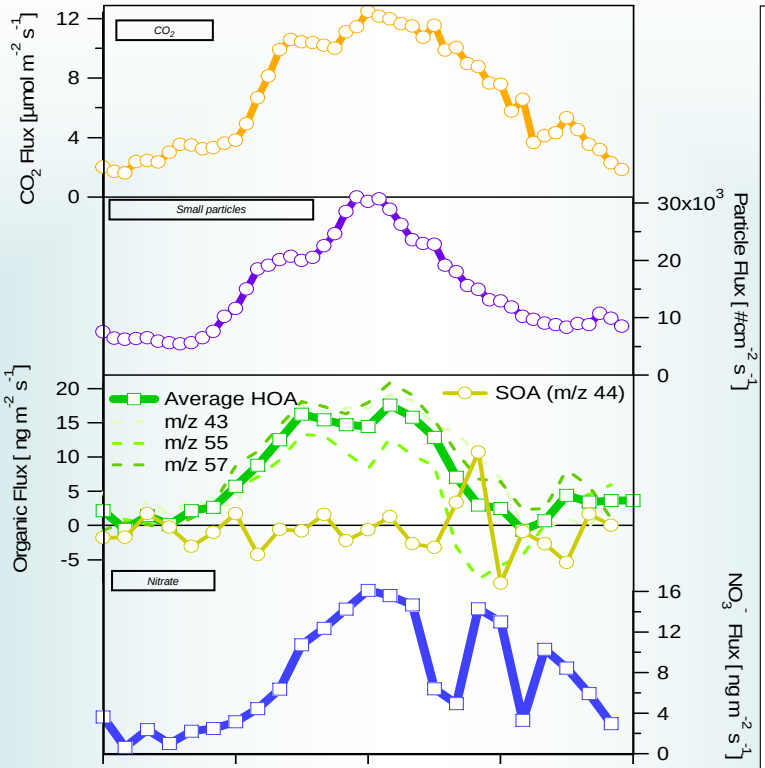
Eiko Nemitz, Rick Thomas, Gavin Phillips, David Fowler

Atmospheric Sciences, Centre for Ecology and Hydrology (CEH), Bush Estate, Penicuik, Midlothian, EH26 0QB, U.K.

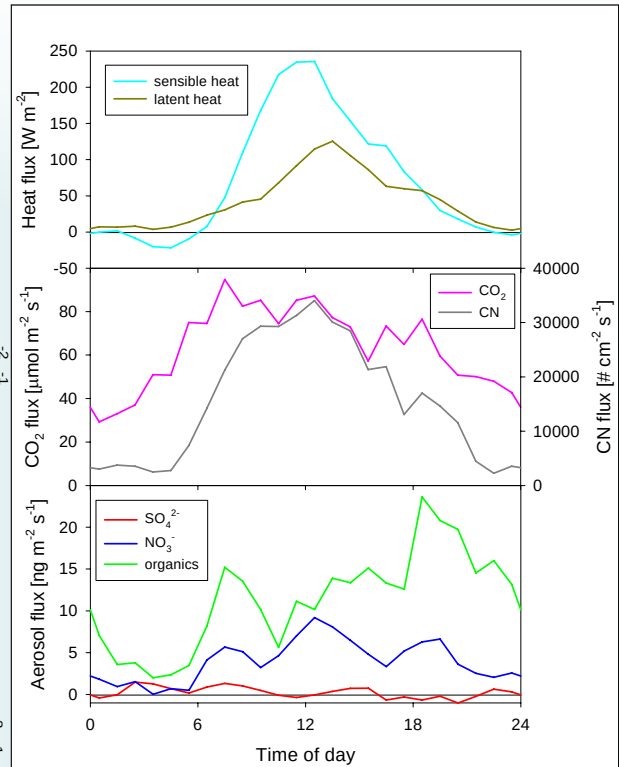


Composition resolved flux measurements using eddy-covariance with an aerosol mass spectrometer reveal urban areas are source of aerosol nitrate.

Gothenburg, Sweden (winter)



Boulder, Colorado (summer)



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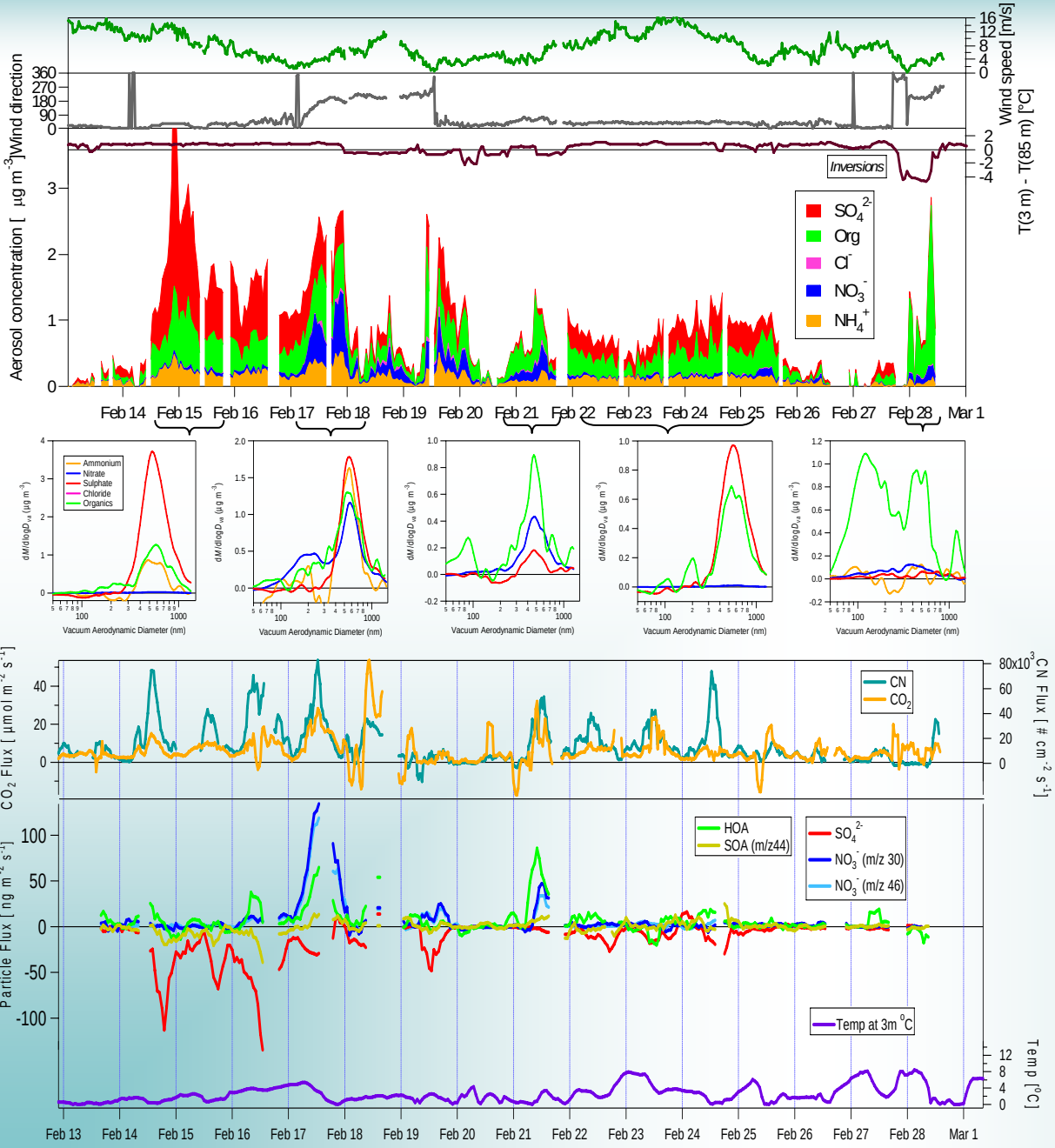

Results:

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- Nitrate formed in urban areas is in the Aitken mode (observed worldwide).
- They occur during both summer and winter, but vary between days.
- In winter emissions appear to be larger on inversion days (build-up of HNO_3 & NH_3?)

Implications:

- Urban areas are important for NOx oxidation.
- Urban areas may be more important for NH_4NO_3 formation than agricultural areas.