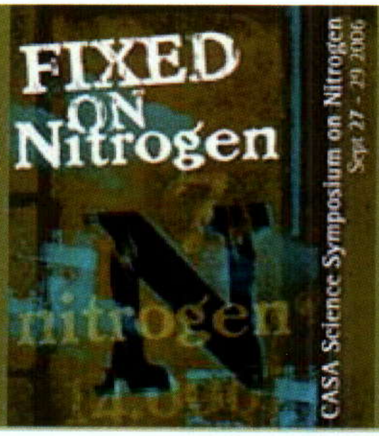

FIXED ON NITROGEN
CASA Science Symposium on Nitrogen
September 27 – 29, 2006
Fairmont Chateau Lake Louise
Lake Louise, Alberta

Abstract

Atmospheric and Depositional Nitrogen Monitoring

Dr. John Neil Cape

The sources of the different forms of nitrogen-containing air pollutants are described as a prelude to asking how and why such pollutants should be measured. Problems of spatial heterogeneity are dealt with by illustrating ways in which concentrations and deposition data can be interpolated and extrapolated from point measurements across a region. New techniques for directly measuring dry deposition fluxes are described, and more appropriate approximate techniques for dry deposition monitoring, based on conditional sampling, are introduced. Inferential modelling of dry deposition, using monitored air concentrations and modelled or measured estimates of atmospheric and surface transport processes, can be used as an alternative to expensive deposition monitoring. The development of low-cost active samplers for trace gases and particles has provided practical approaches to both conditional flux measurements, and improved spatial measurements of air concentrations for use in inferential modelling. The different forms of nitrogen pollutants in the atmosphere are deposited by different processes and at different rates to different vegetation types. For typical concentrations in Alberta, annual dry deposition of nitrogen oxides and ammonia is likely to be at least as important as wet deposition of nitrogen in terms of the overall transfer of nitrogen from the atmosphere to the surface. Estimates of the likely relative magnitude of the different pathways of nitrogen deposition allow priorities to be set for addressing current and future emissions, and indicate where the largest and most important uncertainties currently lie.

Atmospheric and Depositional Nitrogen Monitoring

J N Cape, Y S Tang, R I Smith, M A Sutton, E Nemitz, D Famulari, D Fowler

Centre for Ecology & Hydrology, Edinburgh, UK

CASA Symposium, Lake Louise, Alberta, September 2006

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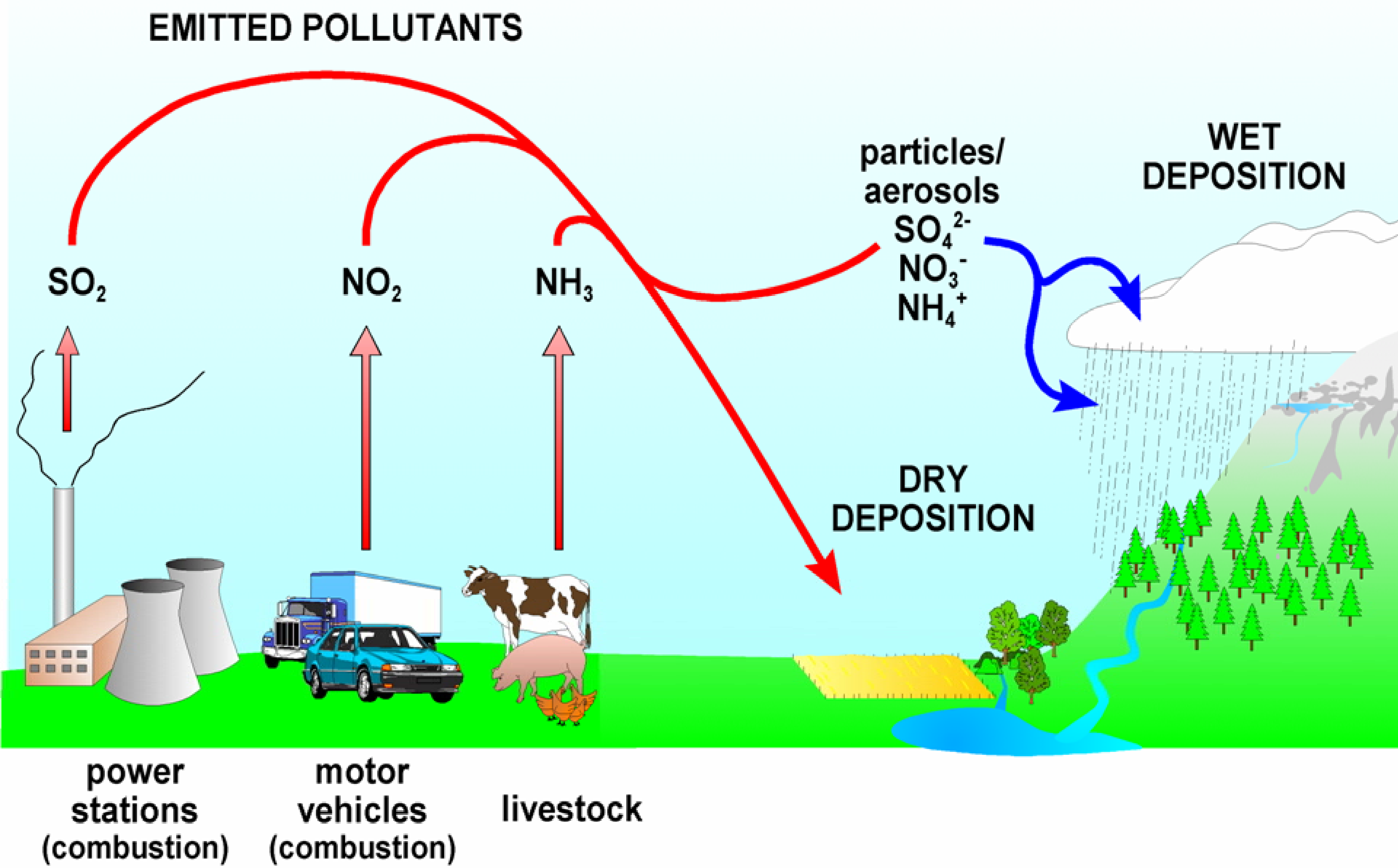
Sources of ‘reactive’ N in the atmosphere

- **What to monitor**

Nitrogen oxides	**NO, NO_2**
Nitric and nitrous acid	**HNO_3, HONO**
Ammonia	**NH_3**
Nitrate and ammonium in aerosols and precipitation	**NO_3^-, NH_4^+**
Organic nitrogen	**various… PAN, urea, amines etc.**

Sources of ‘reactive’ N in the atmosphere

• **What to monitor**	• **Where it comes from**
Nitrogen oxides	Combustion, soil
Nitric and nitrous acid	Oxidation of nitrogen oxides
Ammonia	Animal wastes, senescent vegetation, 3-way catalysts
Nitrate and ammonium in aerosols and precipitation	Oxidation of nitrogen oxides Reaction with ammonia gas Solution of nitrate and ammonium aerosols
Organic nitrogen	Photochemical, possibly agricultural



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How to monitor

Continuous

- Captures short-term variations
- Helps in identification of sources
- Links to dynamic transport models
- Expensive equipment
- Expensive data analysis
- Needs electrical power

Integrating

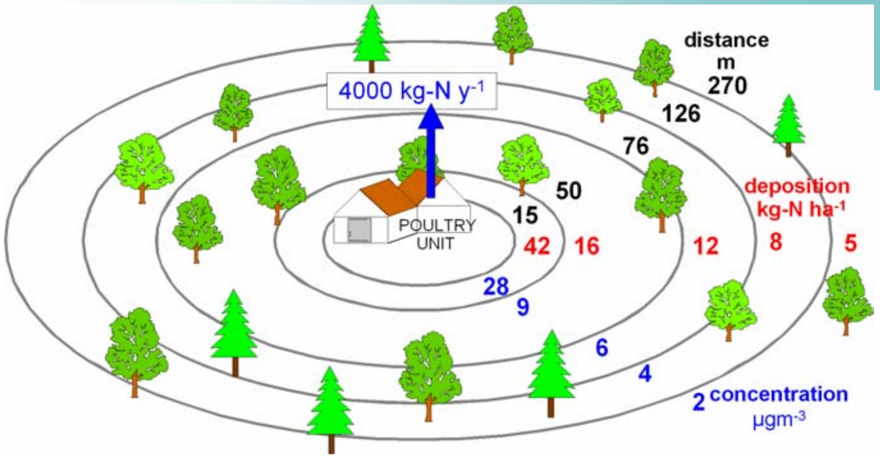
- Good spatial information
- Several components simultaneously
- Matches target load timescales
- Inexpensive equipment
- Needs chemical analysis
- May not need electricity

Why to monitor

Point source

Direct effects on local vegetation and soils

e.g. ammonia from intensive agriculture



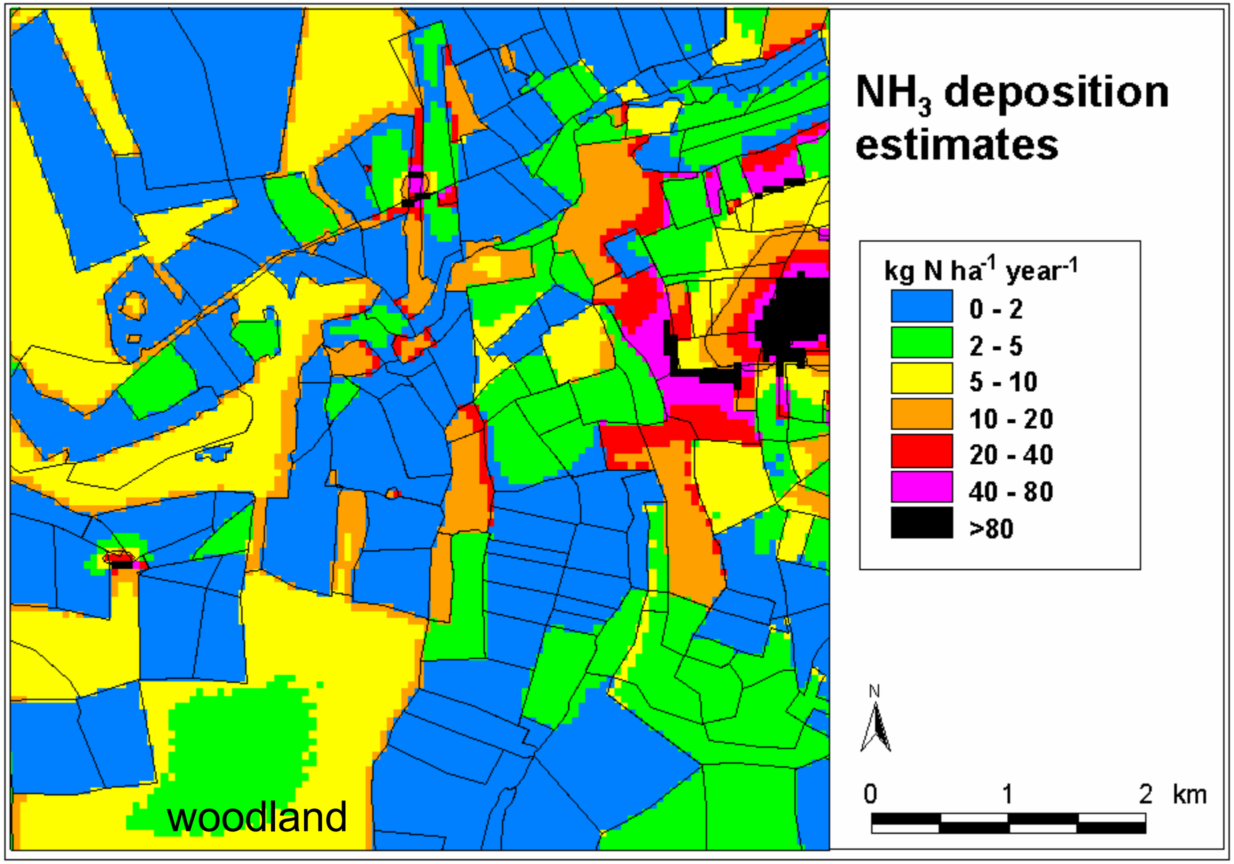
Regional estimate

Comparison with critical loads or target loads

e.g. deposition to sensitive ecosystem

Spatial heterogeneity

- Important close to point sources
- Edges are ‘hot spots’ for deposition



Dragosits et al.
(Environ. Pollution 2002)

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Spatial heterogeneity

- **Important features of the landscape**

  Orographic enhancement of rainfall

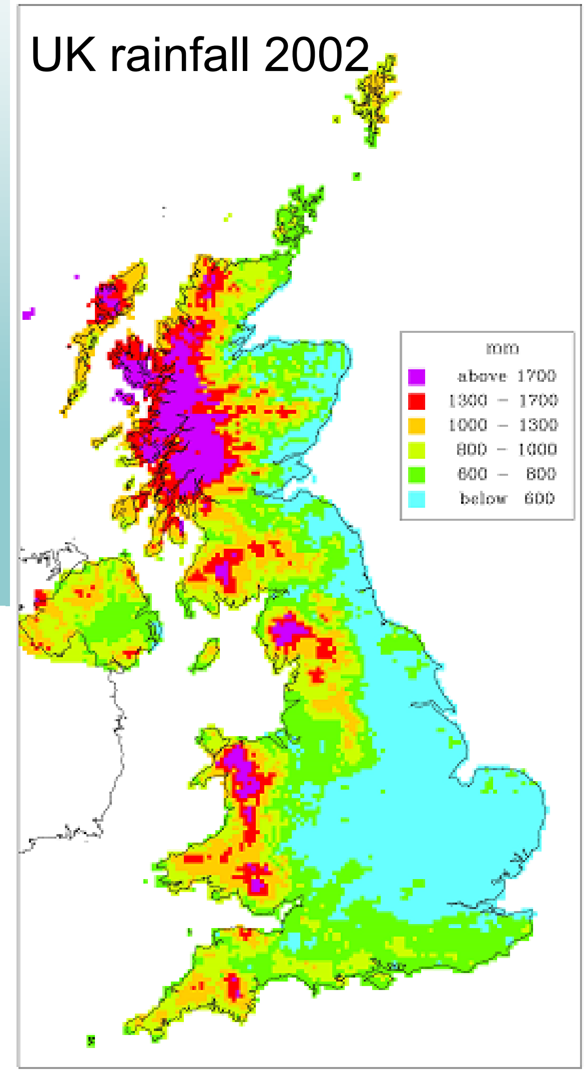
  Deposition in cloud

Spatial heterogeneity

- **Important features of the landscape**

  Orographic enhancement of rainfall

  Deposition in cloud



Deposition monitoring

Wet deposition

- Precipitation amount

Standard rain gauge collects more rain than ‘bulk’ collector

Problems with quantifying snowfall

Standard precipitation amount data are more widely available than chemical data.

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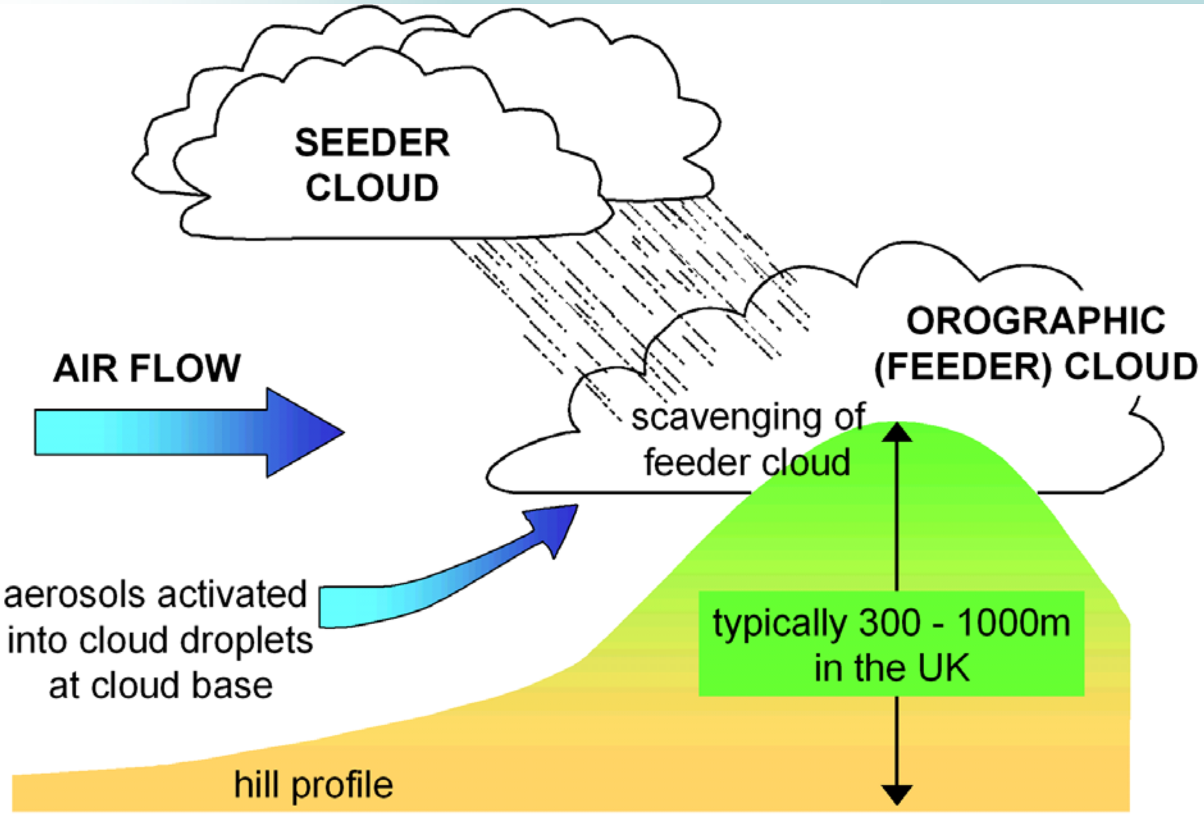
Deposition monitoring

Wet deposition

- Cloud – is it an issue?



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Deposition monitoring

Wet deposition

- 'Bulk' or 'wet-only' ?

Bulk:
Inexpensive
No power
Many replicates

Wet-only:
Less contamination
Preserved samples

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Deposition monitoring

Wet deposition

- ‘Bulk’ or ‘wet-only’ ?

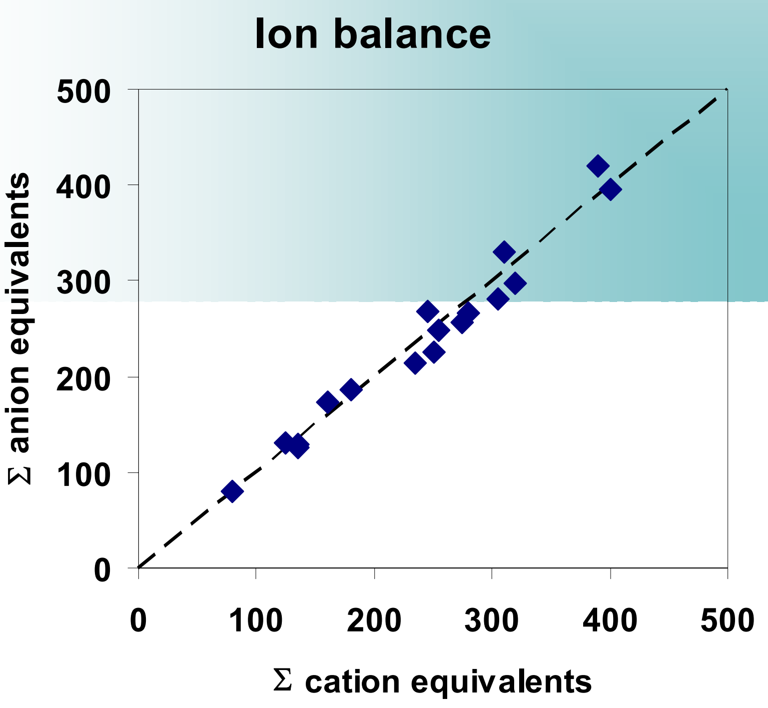
Bulk:
Contamination
Sample storage

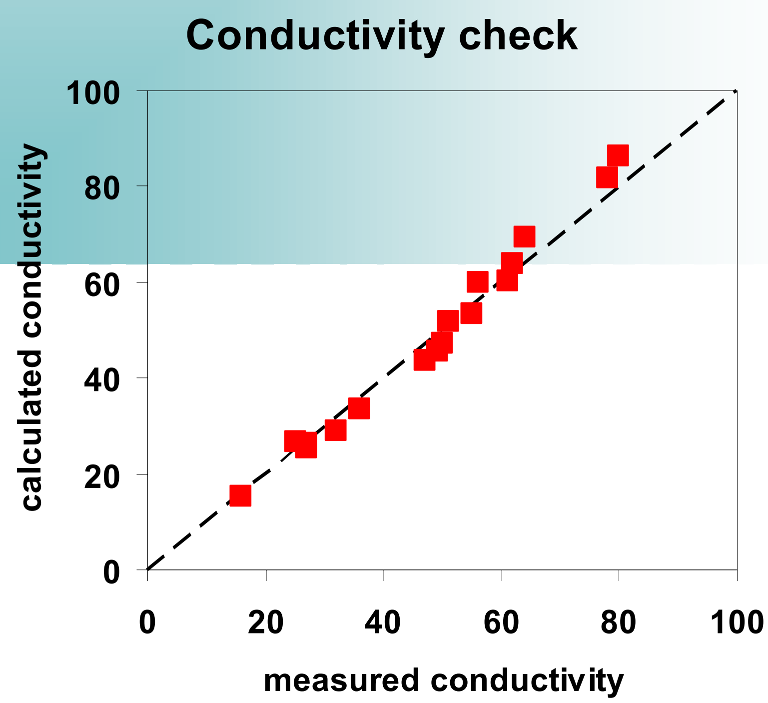
Wet-only:
Not artefact-free
Problems with amounts
Needs electricity
Expensive

Deposition monitoring

Wet deposition

- Quality control - check for contamination (K, P)
- Missing values - use predictions to fill gaps





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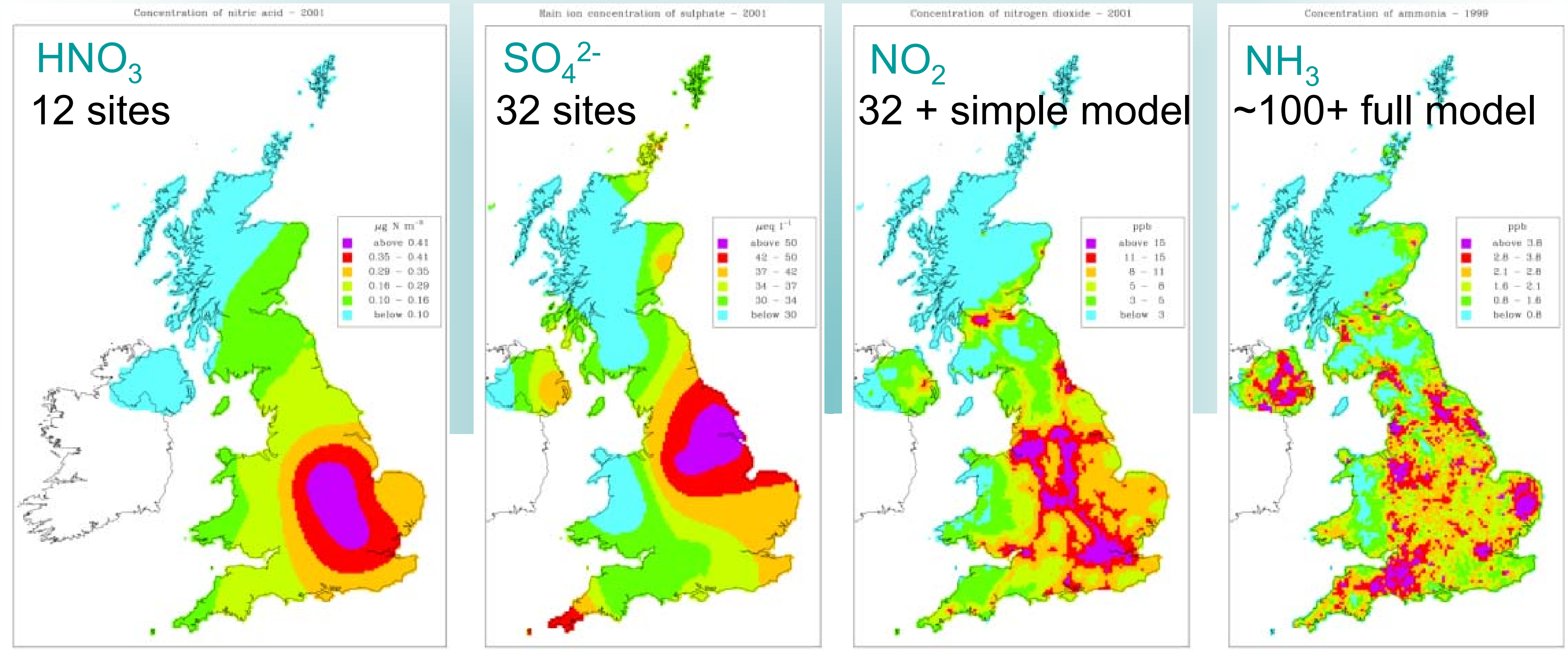
Interpolation and extrapolation

generating a concentration map



more sites gives more definition ($HNO_3 \rightarrow SO_4^{2-}$)
extra information improves structure ($SO_4^{2-} \rightarrow NO_2 \rightarrow NH_3$)

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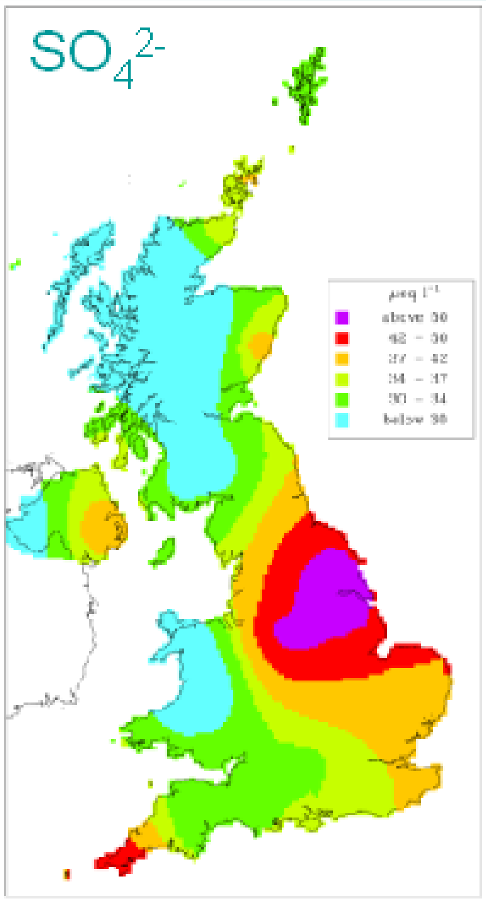
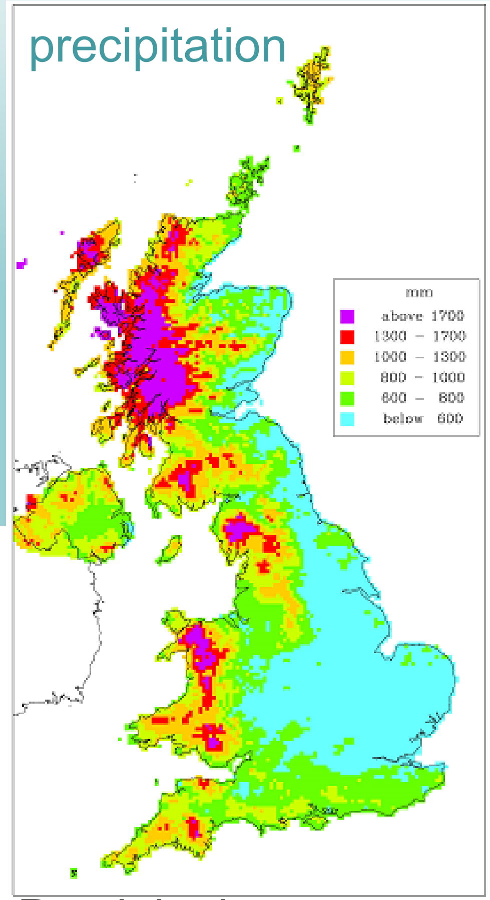
Interpolation and extrapolation

generating a deposition map



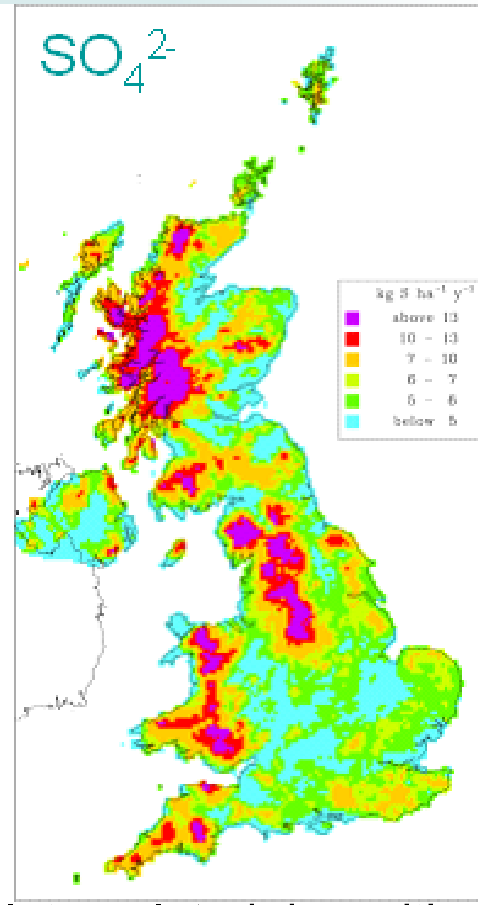
Interpolated concentration

x



Precipitation amount

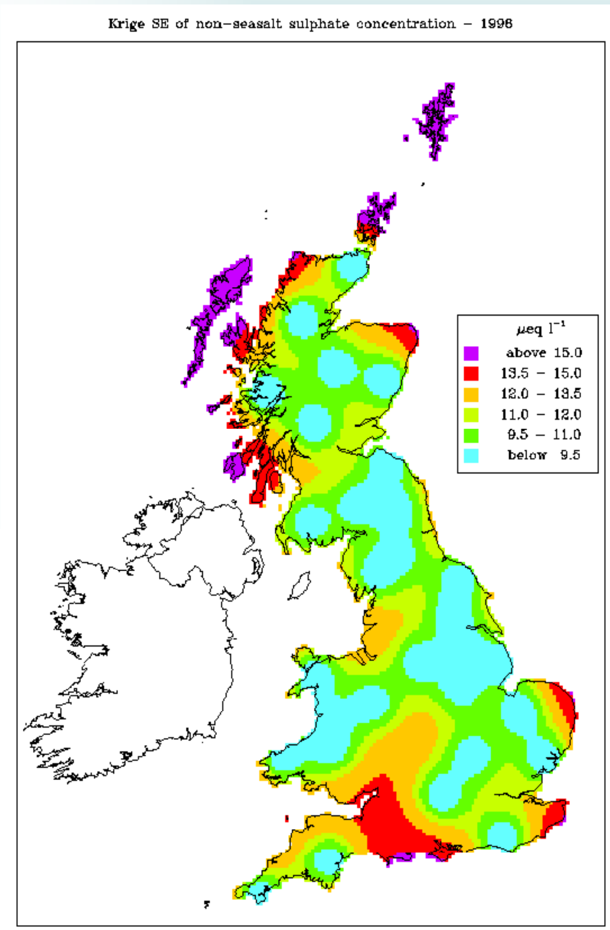
=>



Interpolated deposition

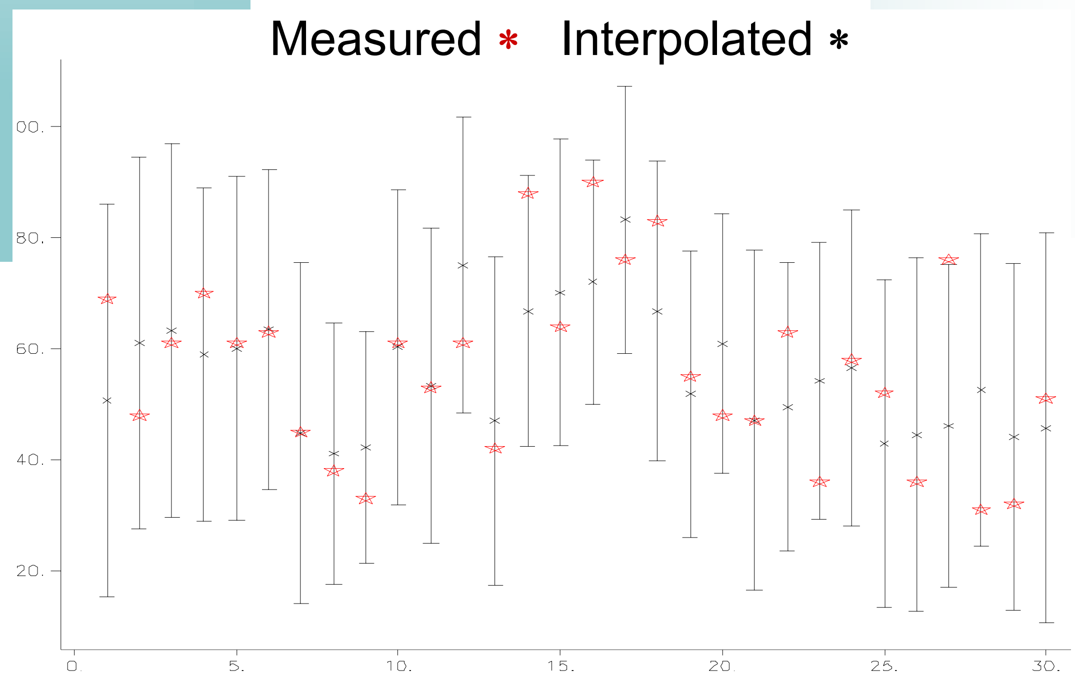
Interpolation and extrapolation

- **Uncertainty estimates**



30 site network for non-seasalt SO_4^{2-} in 1996

Map of kriged standard error and results of cross-validation study (predicted mean for omitted sites with 95% confidence intervals)



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Deposition monitoring

Wet (+ dry) deposition

- Throughfall measurements
  - good for estimating deposition of conserved species (e.g. sulphate) provided sampling design is adequate
  - only works for forests
  - unreliable for non-conserved species, e.g. ammonium and nitrate

Deposition monitoring

Dry deposition

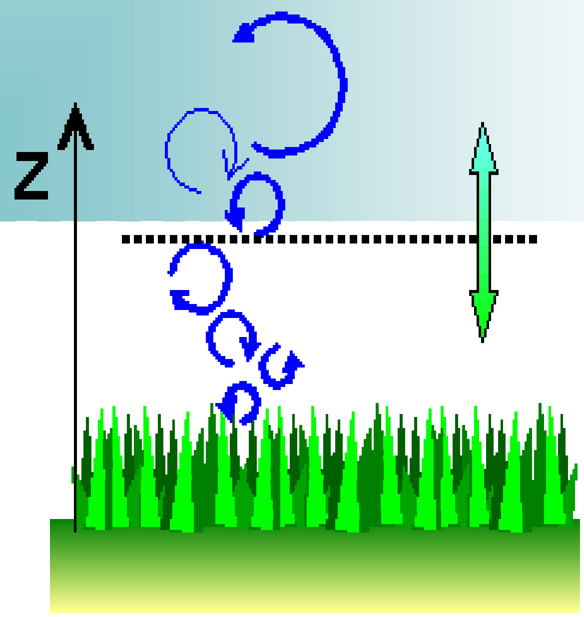
- Direct measurement

$$\text{flux}\chi = \overline{w'\chi'}$$

w' - fluctuation in vertical wind speed

χ' - deviation from mean concentration

Need to measure the **flux** of a gas or particles from the atmosphere to the surface, or *vice versa.*



Transport occurs through atmospheric turbulence and diffusion.

Deposition monitoring

Dry deposition

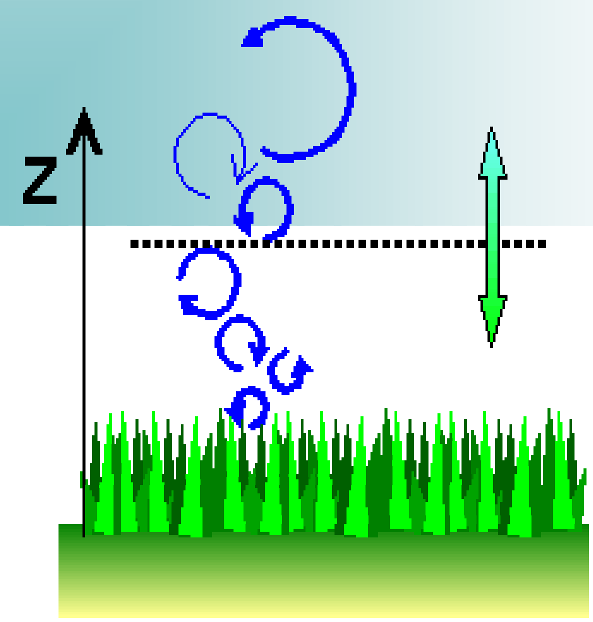
•Direct measurement

$$\text{flux}\chi = \overline{w'\chi'}$$

w' - fluctuation in vertical wind speed

χ' - deviation from mean concentration

In practice this means measuring separately the concentration in the upward-moving eddies and the downward-moving eddies.



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Deposition monitoring

Dry deposition

•Direct measurement

To capture the eddies we need fast (10 Hz) measurements of wind speed and direction, and simultaneous fast measurements of the concentration

sonic anemometer

gas inlet

Deposition monitoring

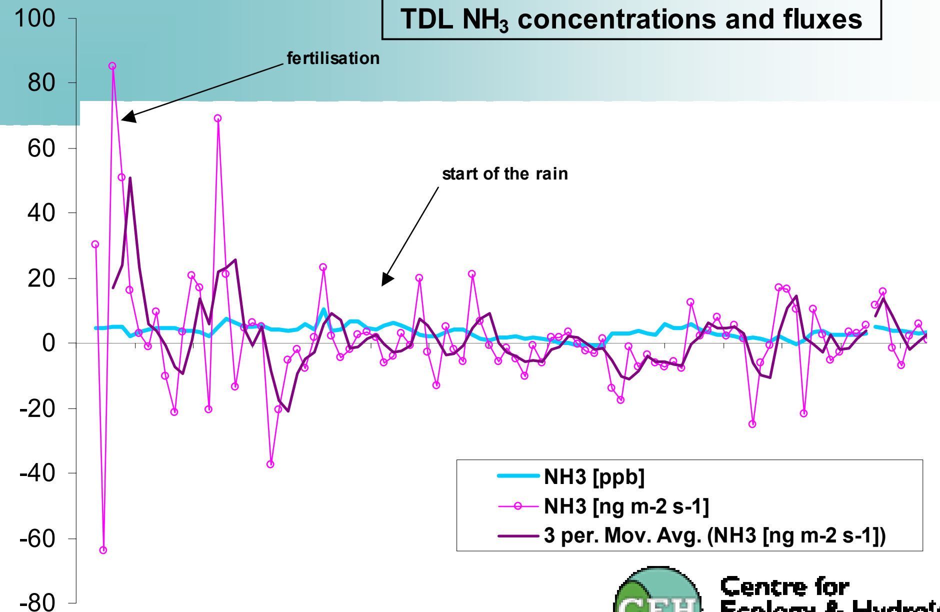
Dry deposition

•Direct measurement

The analytical detectors are expensive, e.g. tunable diode lasers.

Real-time fluxes allow us to understand the processes controlling deposition.

Easter Bush, August 10th-11th, 2002
TDL NH_3 concentrations and fluxes



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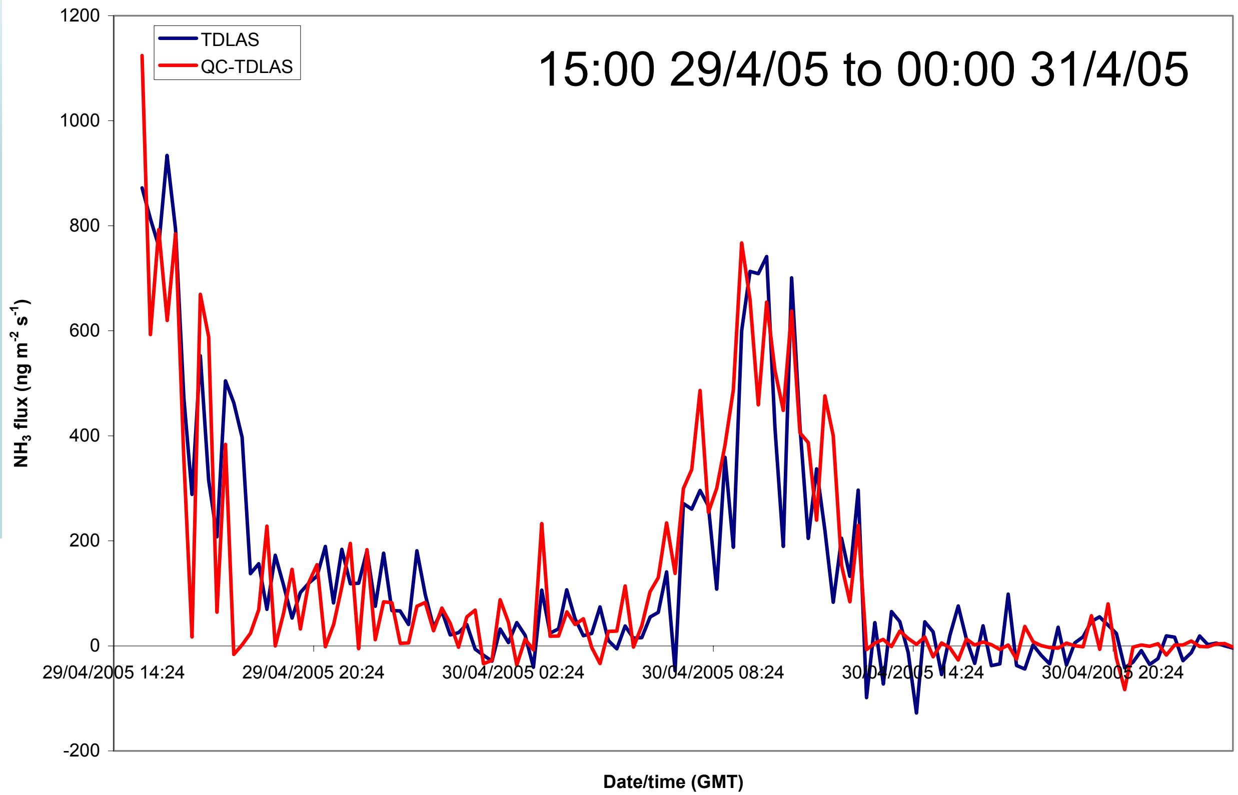
Deposition monitoring

First Intercomparison of TDL-AS for NH_3 fluxes

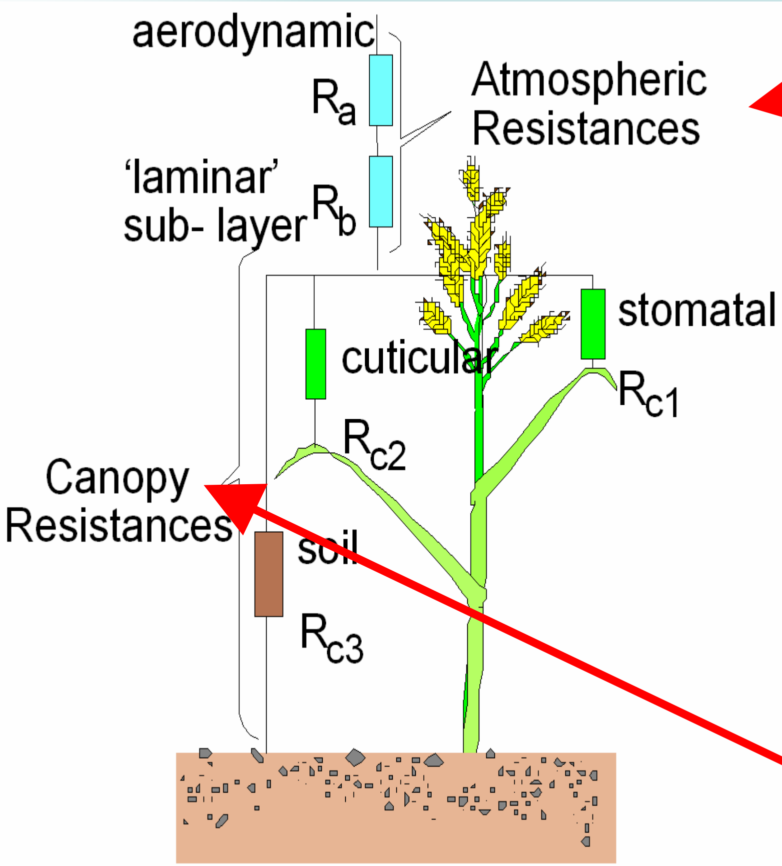


Eddy covariance for NH_3 now possible – but still not easy

Deposition monitoring

Dry deposition

- Understanding the processes



Depend on wind speed and turbulence

$$v_d = \frac{\text{flux}}{\text{concentration}} = \frac{1}{R_t}$$

$$R_t = R_a + R_b + (1/R_{c1} + 1/R_{c2} + 1/R_{c3})^{-1}$$

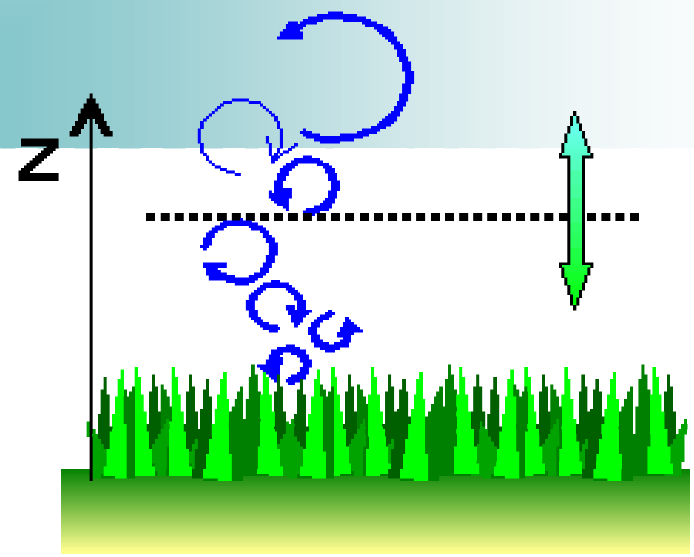
Depend on properties of the surface

Deposition monitoring

Dry deposition

- Indirect measurement – eddy accumulation

A fast-switching valve is used to direct air from upward- and downward-moving eddies into separate “containers” which can be analysed slowly.

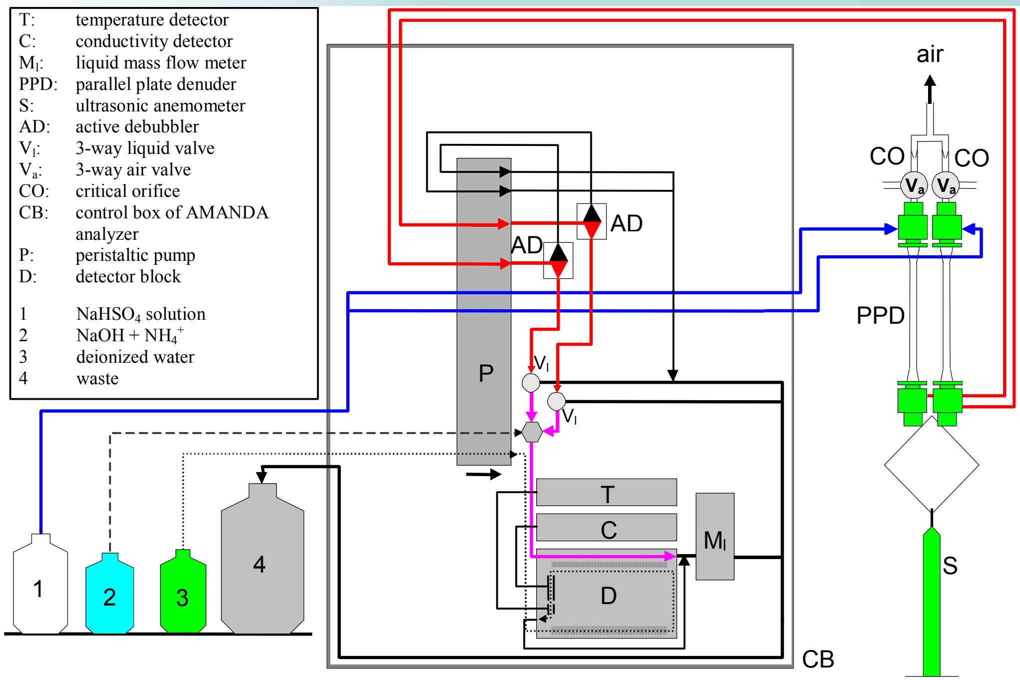


Time resolution is ~ 30 min.

Deposition monitoring

Dry deposition

- Indirect measurement – eddy accumulation



Continuous relaxed eddy accumulation (REA) system for NH_3

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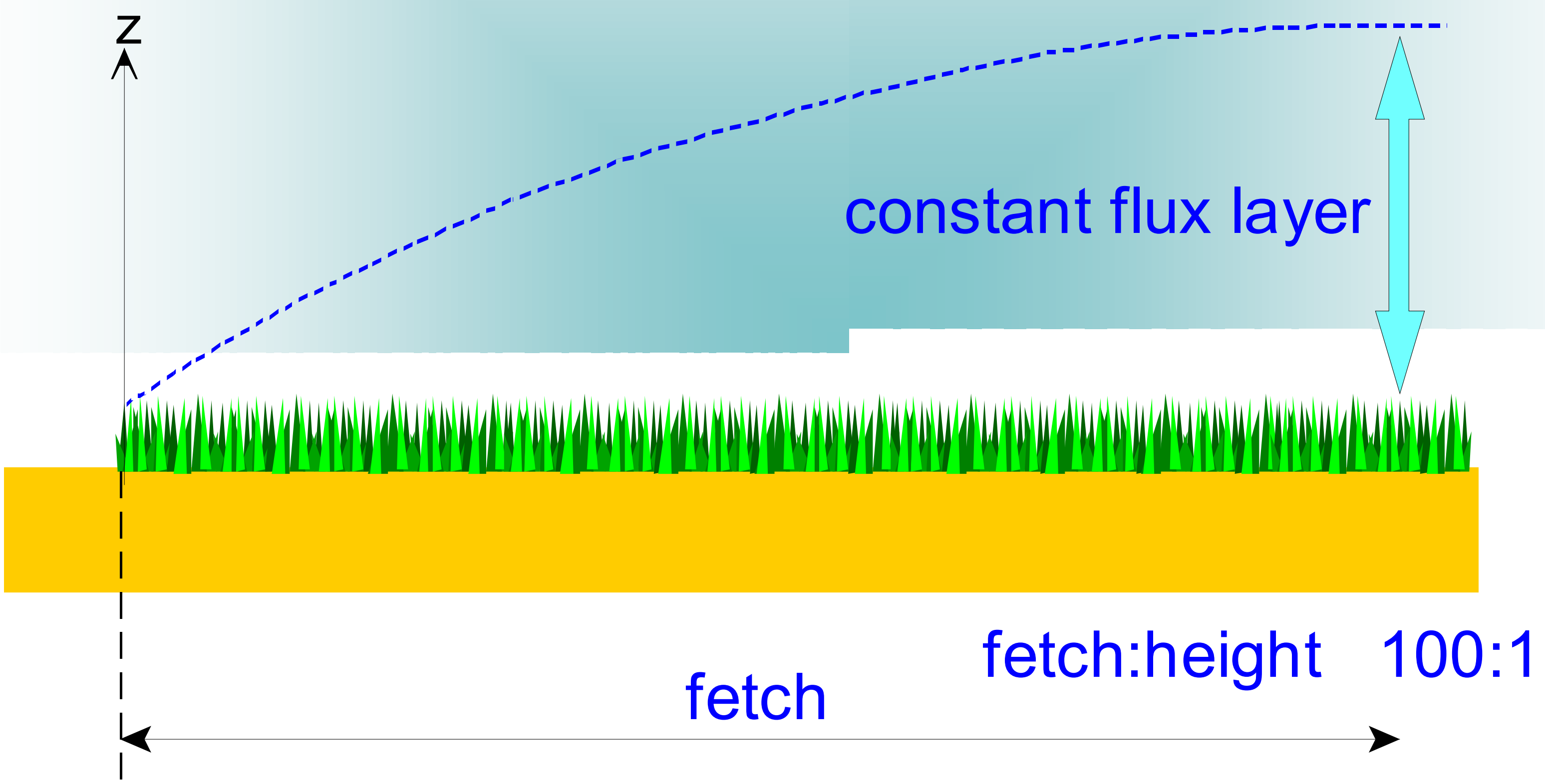
Deposition monitoring

Dry deposition

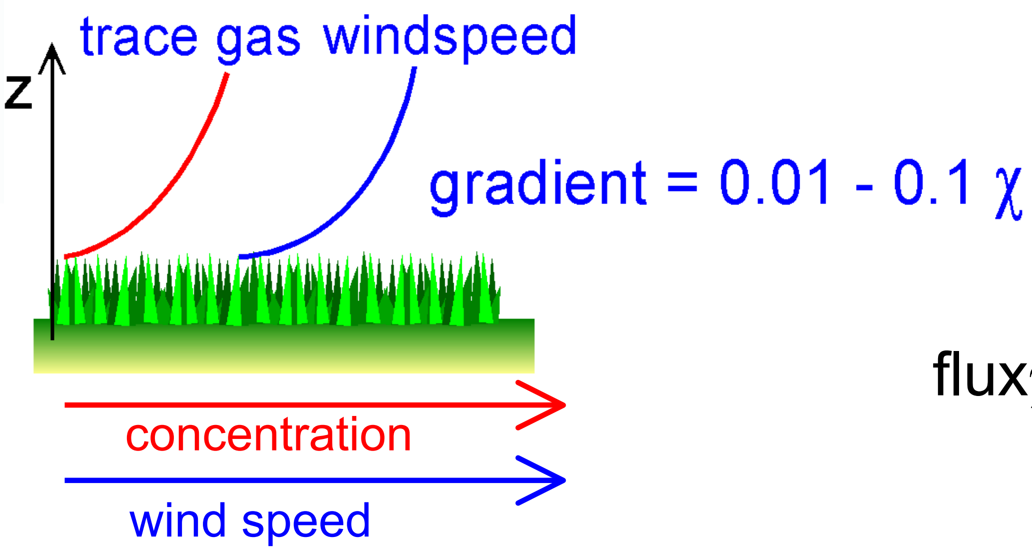
- Indirect measurement – flux gradient



Deposition monitoring

Dry deposition

- Indirect measurement – flux gradient



$$\text{flux}\chi = K\chi \frac{\partial \chi}{\partial z}$$

with stability correction:

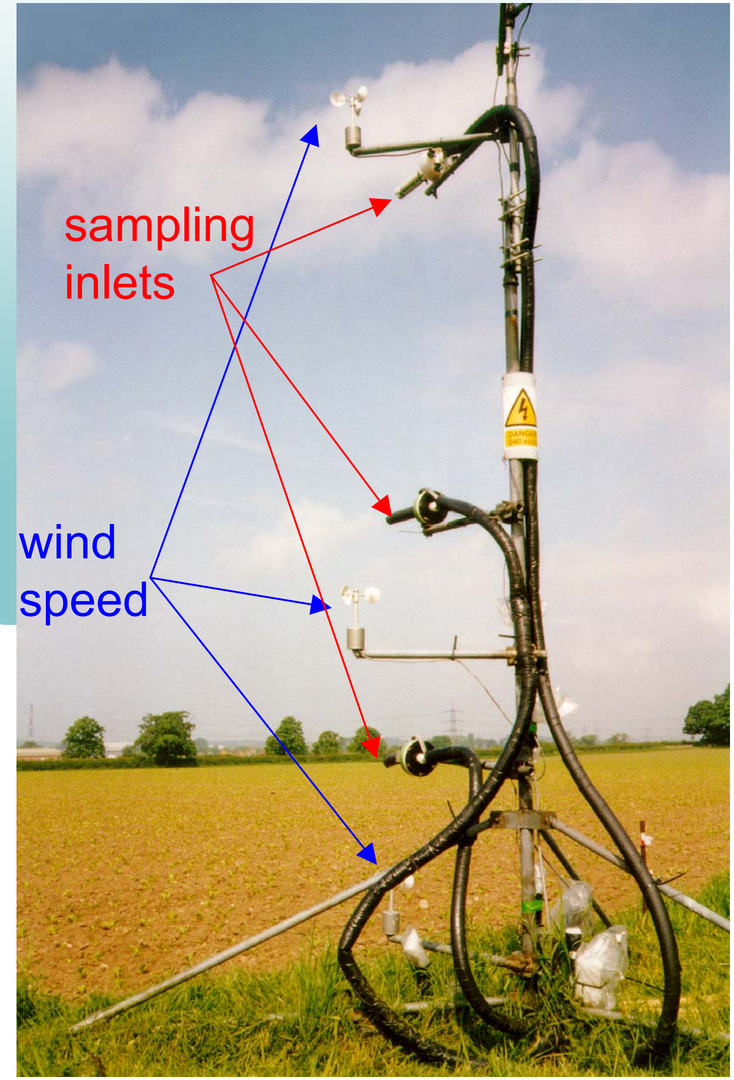
$$\text{flux}\chi = k u_* \frac{\partial \chi}{\partial[\ln(z-d) - \Psi_H\{\varsigma\}]}$$

Deposition monitoring

Dry deposition

- Indirect measurement – flux gradient

- Typical 30 min data.
- Requires adequate fetch and wind speed.
- Theory does not work under some conditions.
- Can use ‘slow’ analyzer
- Data processing takes a long time



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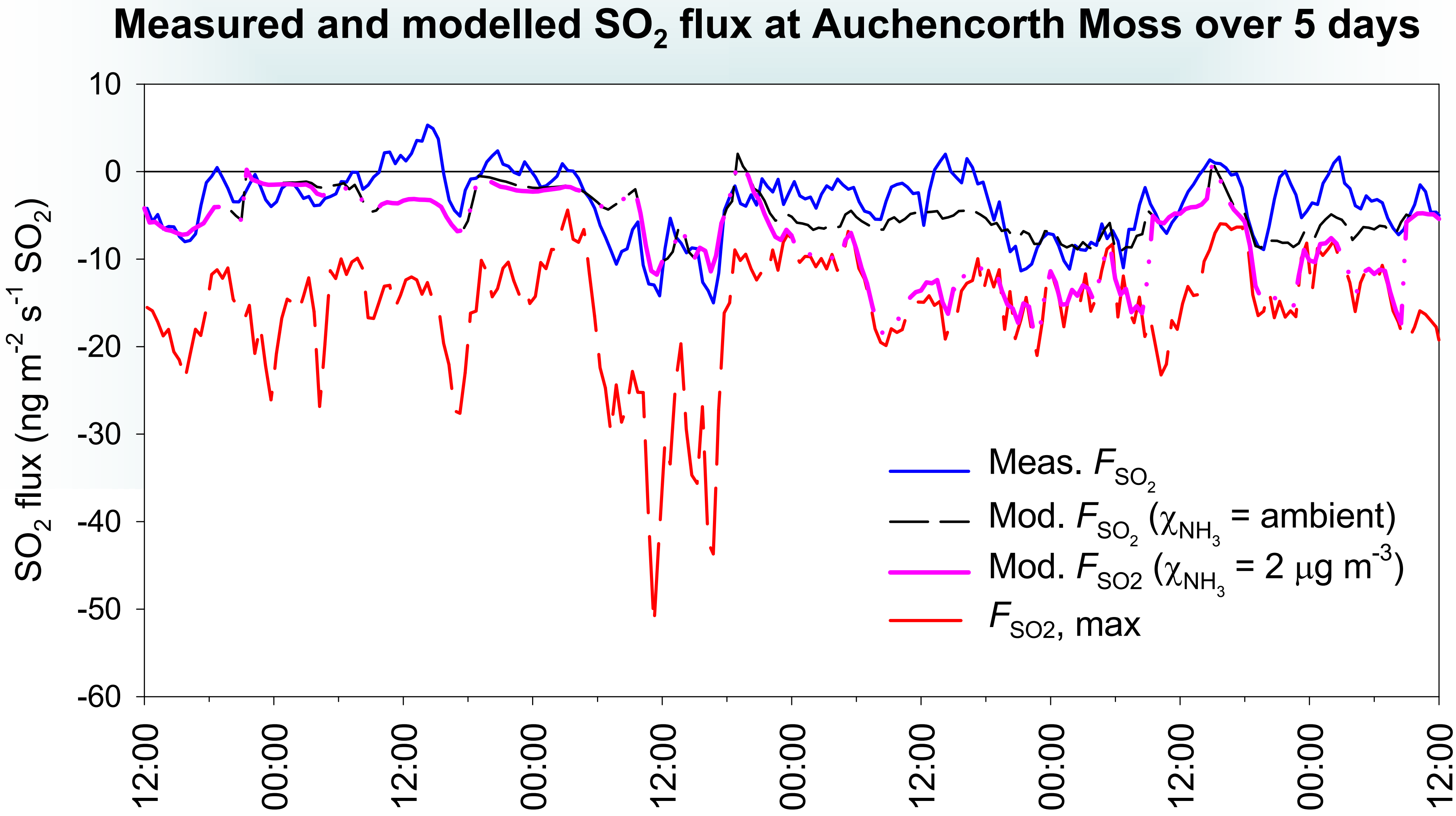
Deposition monitoring



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Deposition monitoring

Dry deposition – comparison of measurements

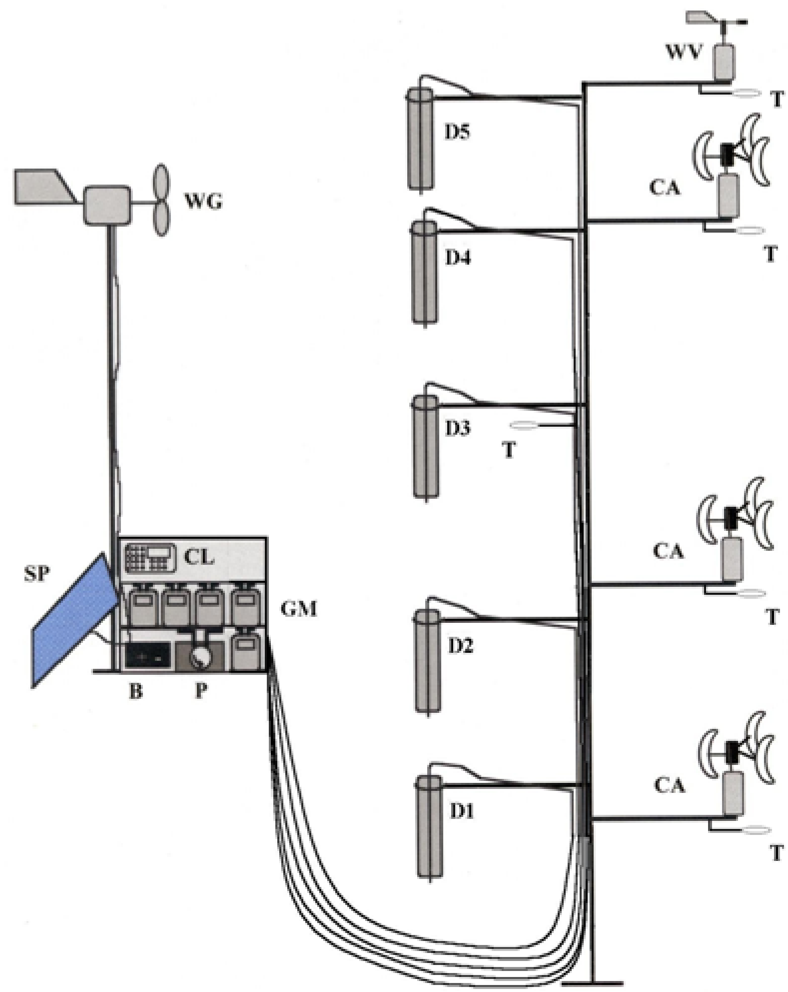
	Eddy covariance	Flux gradient
Equipment cost ($)	2-500,000	~ 20,000
Equipment maintenance	Labour intensive	Automated
Skills required	Post-doc	Graduate
Time resolution	second	hour
Data processing	Labour intensive	Moderate

Deposition monitoring

Dry deposition

- **Conditional time-averaged gradient (COTAG)**

- 1-4 week averaged flux of NH_3, SO_2 (and other trace species, e.g. particles)
- Concentration and turbulence, temperature, wind direction, stability, heat flux also provided



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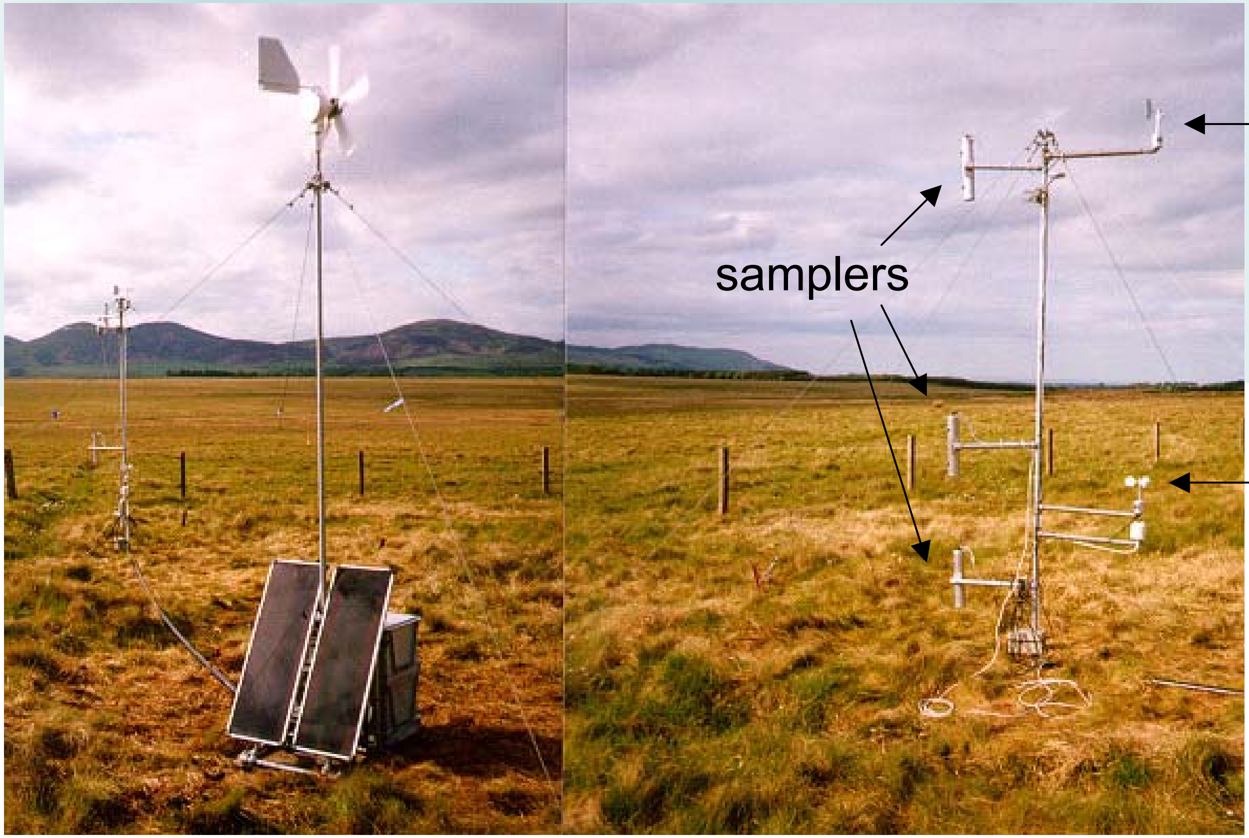
Deposition monitoring

Dry deposition

- **Conditional time-averaged gradient (COTAG)**

wind and
solar
powered



samplers

wind
direction

wind
speed

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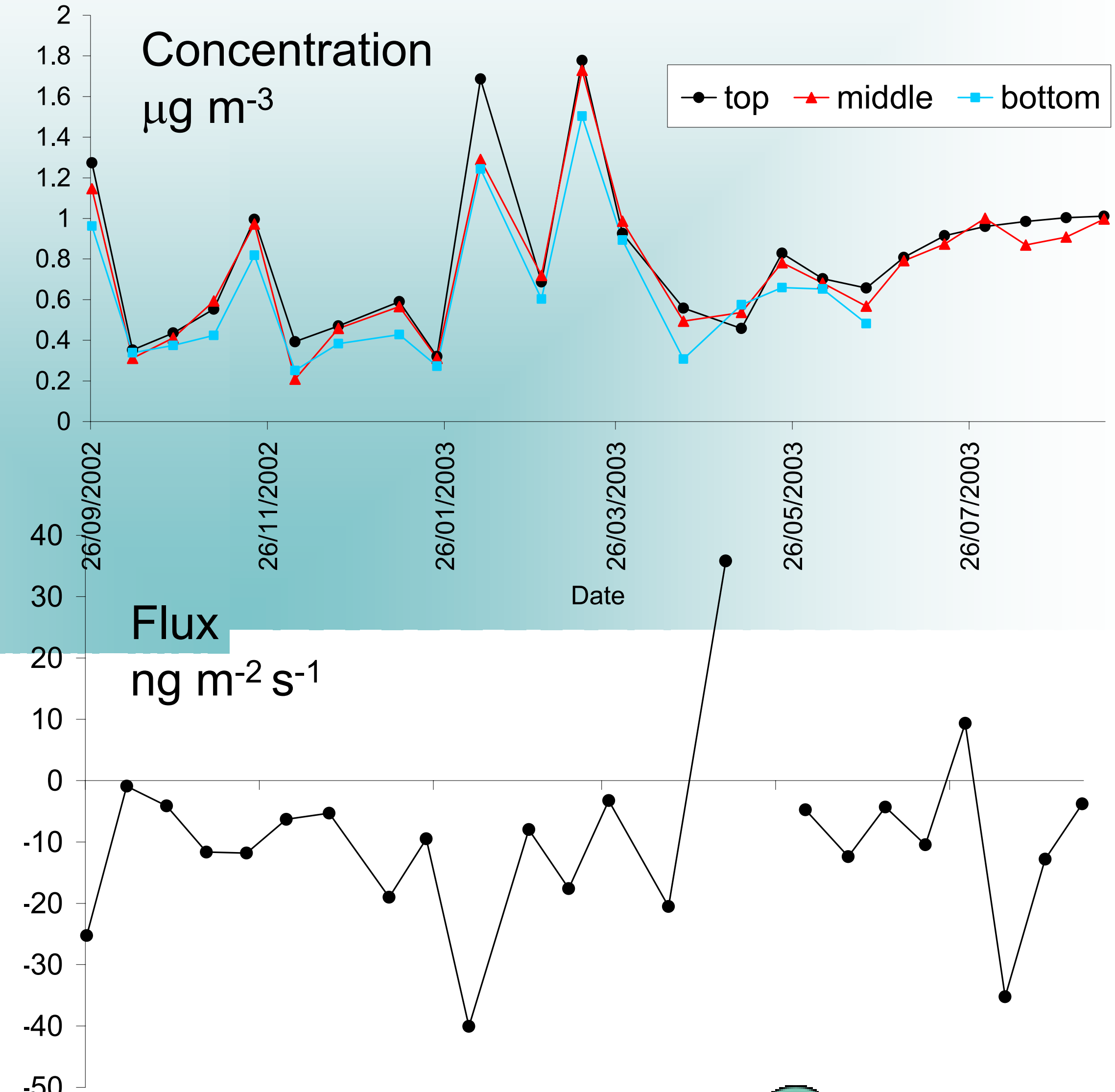
Deposition monitoring

Dry deposition

- **Conditional time-averaged gradient (COTAG)**

Two-weekly measurements of ammonia fluxes at Auchencorth Moss: Sep 02 – Aug 03



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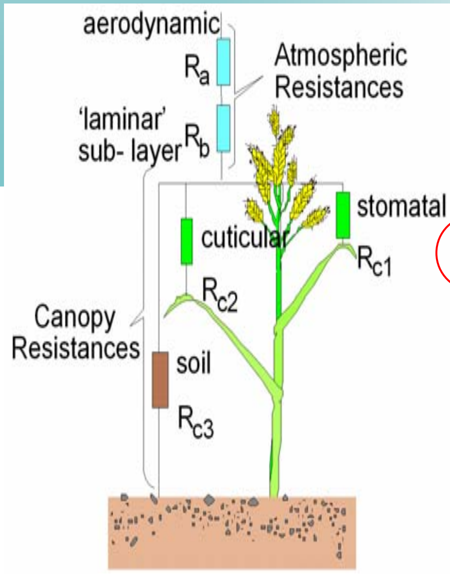
Deposition monitoring

Dry deposition

- Inferential methods

Combine measured or modelled concentrations with measured or modelled deposition velocities (v_d):

flux = v_d *x concentration*



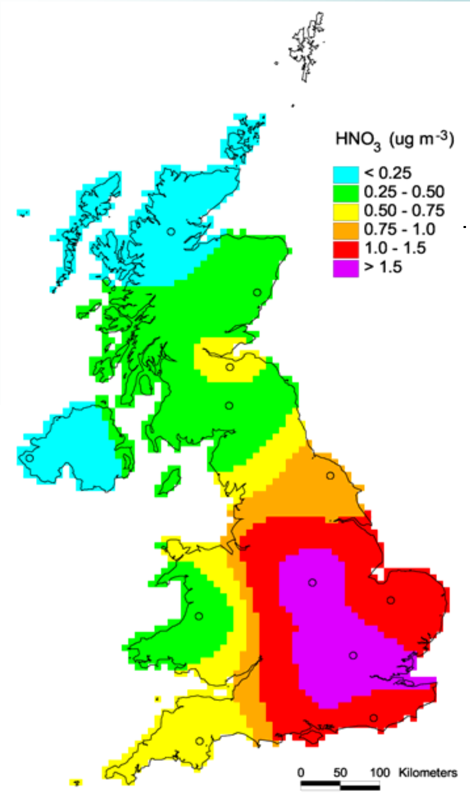
$$v_d = \frac{\text{flux}}{\text{concentration}} = \frac{1}{R_t}$$

$$R_t = R_a + R_b + (1/R_{c1} + 1/R_{c2} + 1/R_{c3})^{-1}$$

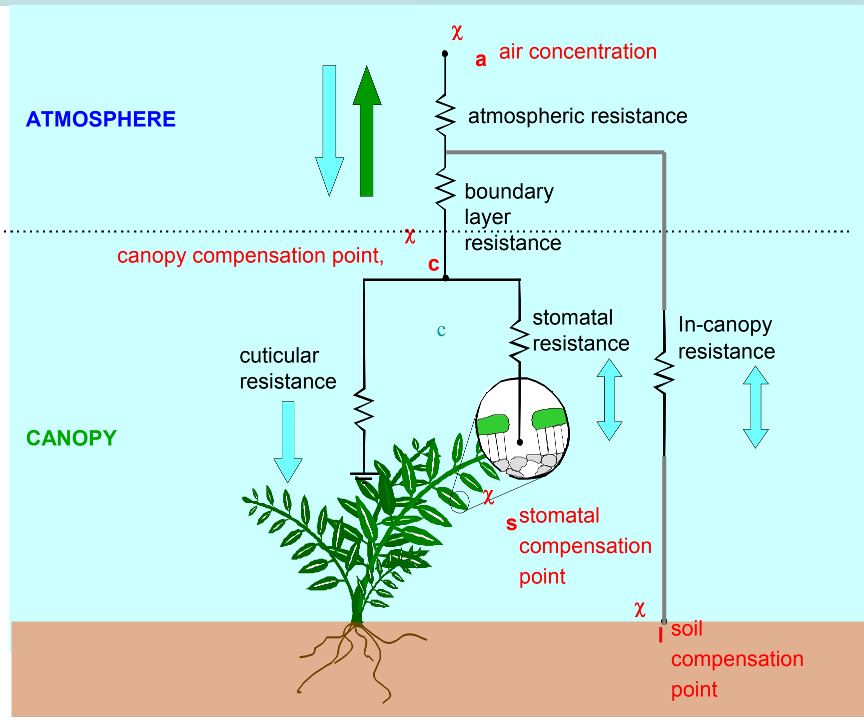
Deposition monitoring

Dry deposition - Inferential methods

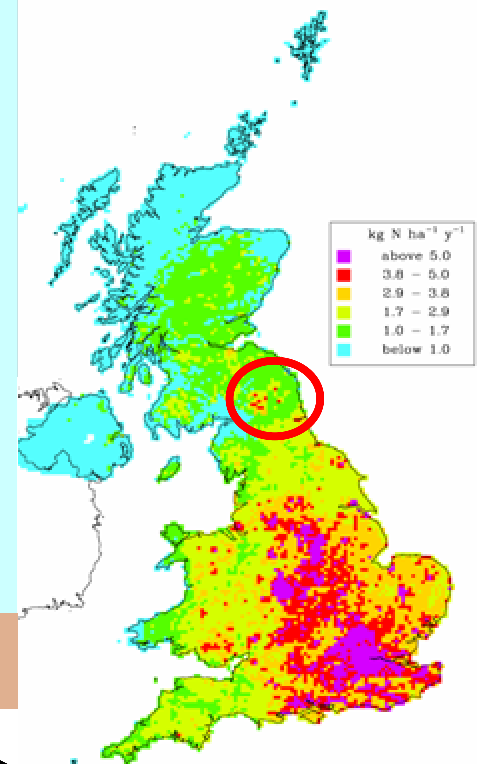
HNO_3 concentration



Deposition model



HNO_3 deposition



Depends on land use / vegetation

Deposition monitoring

Dry deposition - Inferential methods

Measured concentration + modelled depn velocity

spatially interpolated	**vegetation dependent**
annual average	annual average
monthly average	seasonal variation
hourly average	based on measurements

Vegetation dependence involves seasonal changes in:

- vegetation height (roughness)
- leaves present/absent
- foliage active/dormant

Wind speed dependence of deposition velocity can be based on measurements

Concentration monitoring

- Continuous gas analyzers

  Useful for near-source 'acute' exposure estimates and source attribution, but expensive for area estimates

- Integrating methods

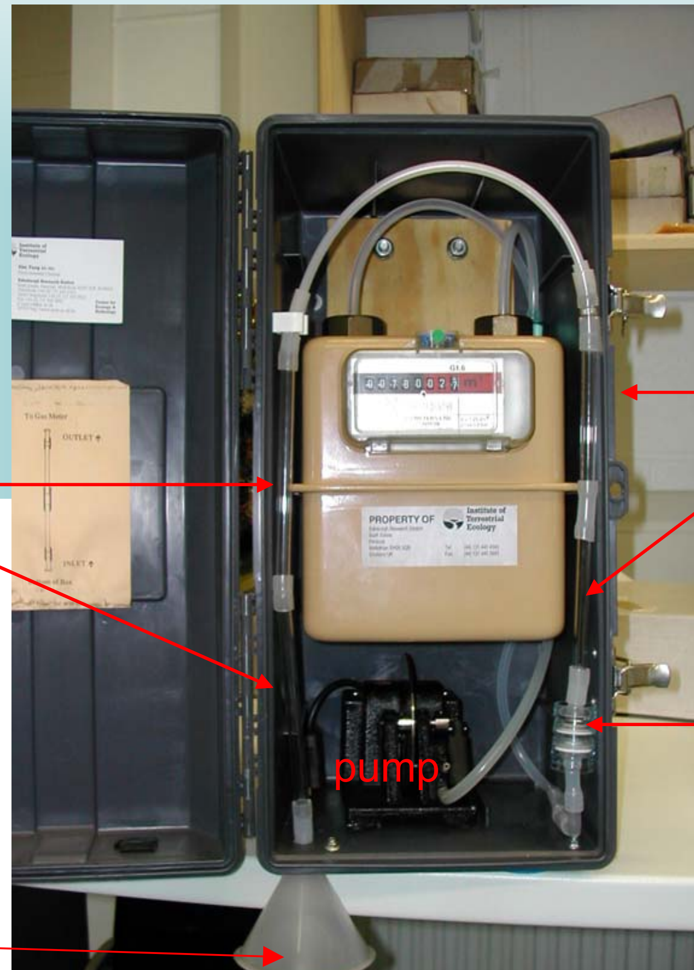
  Active methods require power (but may be wind/solar)

  Passive methods do not

  Both can provide data adequate for deposition estimation

Concentration monitoring

- Low-cost active monitoring of trace gases and aerosols (**DELTA**)



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

Shorter denuders 3 + 4
To remove NH_3

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

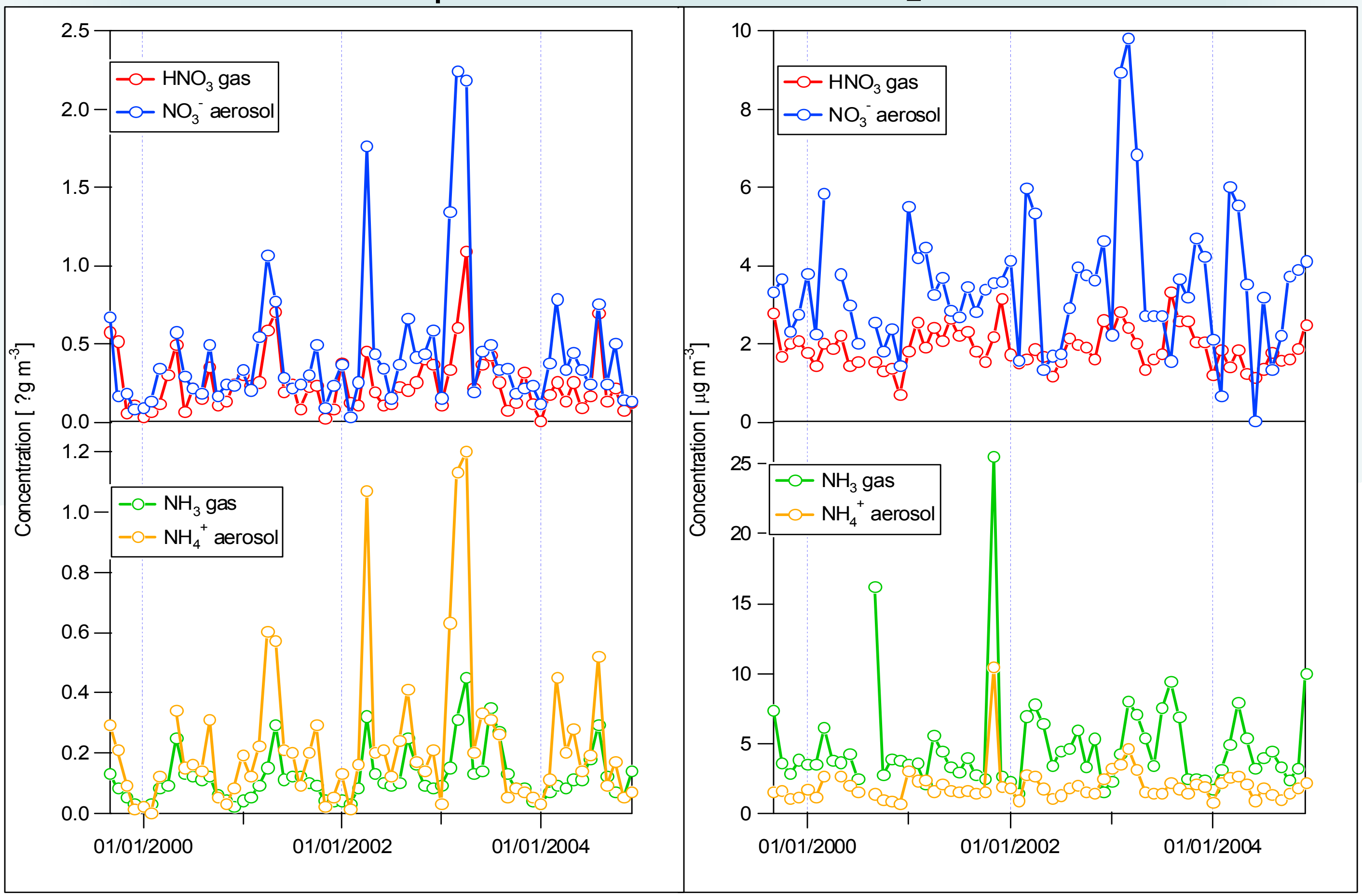
Air inlet

Concentration monitoring

Example time series of monthly monitoring

Strathvaich Dam
Remote Scottish Upland Site

Sutton Bonington
SO_2 Source Region



1999 - 2005

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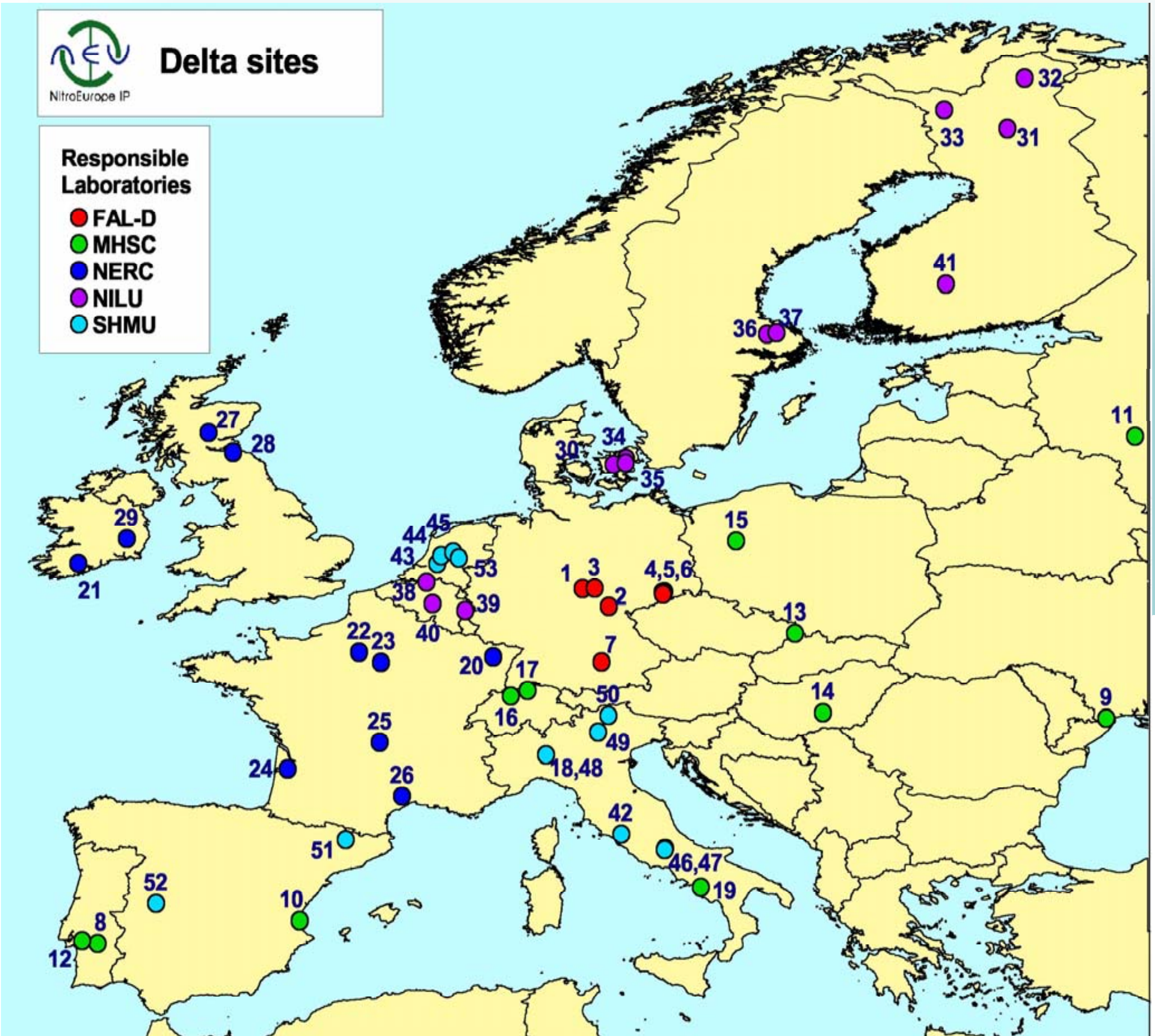
Implementation in NitroEurope

NitroEurope IP



● **<u>'Level 1' (50 sites)</u>**
continuous concentration measurements (**DELTA**) and measured atmospheric turbulence

\+ **<u>'Level 2' (9 sites)</u>**
continuous flux measurements
using COTAG systems

\+ **<u>'Level 3' (13 sites)</u>**
continuous flux measurements using eddy covariance and/or gradient techniques

www.neu.ceh.ac.uk

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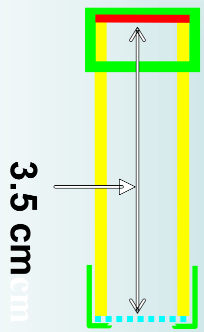
Concentration monitoring

Passive sampling – examples for ammonia

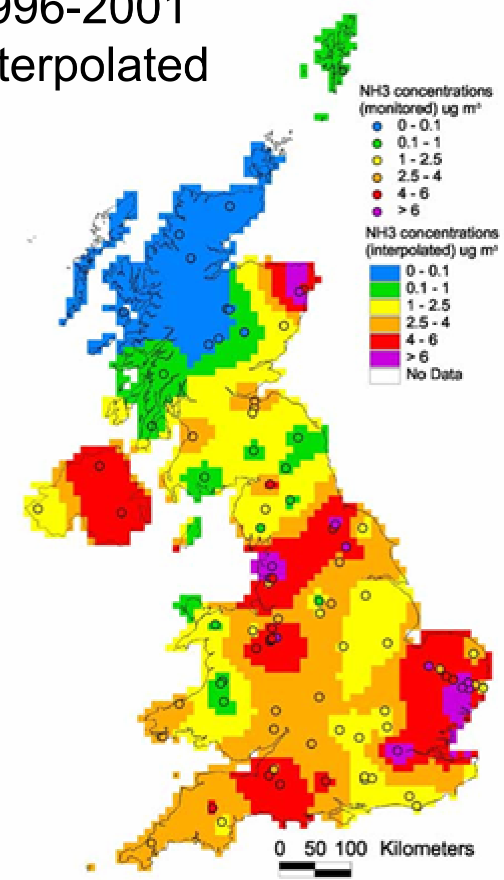


Passive diffusion tube with membrane to reduce effects of wind turbulence

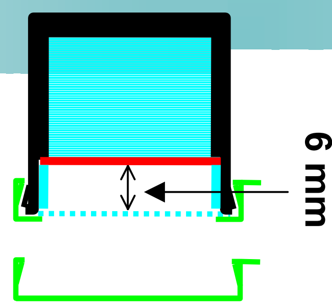
Slow sampling rate

3.5 cm
Membrane
DT

1996-2001
interpolated



CEH ALPHA sampler
Fast sampling rate



KEY
- Impregnated filter / grid
- Membrane

Use of models to estimate deposition

How do we assess uncertainty?

- Comparison with measurements –
  but beware of comparing point measurements with area estimates, even at 1 km x 1 km.
- Sensitivity analysis –
  which model parameters are critical?
- Typical uncertainties are factor 2 for individual 20 x 20 km grid annual deposition estimates.

Priorities for Alberta

Wet deposition

- Ammonium-N: 0.2 – 2 kg N ha^{-1} y^{-1}
- Nitrate-N: 0.1 – 1 kg N ha^{-1} y^{-1}
- **Inorganic-N: 0.3 – 3 kg N ha^{-1} y^{-1}**
- Organic-N: ?

Concentrations 0.1 – 1 mg N $litre^{-1}$

Precipitation 150 – 600 mm y^{-1}

Priorities for Alberta

Dry deposition

Concentrations

- Ammonia : 1 – 20 μg m^{-3} (median 5)
- Nitric acid : ? 0.3 μg m^{-3}
- Nitrogen dioxide : 2 – 60 μg m^{-3} (median 12)
- Particulate nitrate: ? 1 μg m^{-3}

[www.casadata.org; Peake et al., 1988]

Deposition velocities

- Ammonia : 0 – 10 cm s^{-1} (SO_2, wetness)
- Nitric acid : 0.5 – 10 cm s^{-1} (no surface resist.)
- Nitrogen dioxide : 0.1 – 0.3 cm s^{-1} (stomatal)
- Particulate nitrate: 0.01 – 1 cm s^{-1} (size dependent)

Priorities for Alberta

Dry deposition

Concentrations x deposition velocities

- Ammonia : 0 – 50 (rural 1-5) kg N ha^{-1} y^{-1}
- Nitric acid : ? 1 kg N ha^{-1} y^{-1}
- Nitrogen dioxide : 0.3 – 9 (median 2) kg N ha^{-1} y^{-1}
- Particulate nitrate: ? <1 kg N ha^{-1} y^{-1}

Total dry N deposition: **several** kg N ha^{-1} y^{-1}

cf. wet deposition **0.3 – 3** kg N ha^{-1} y^{-1}

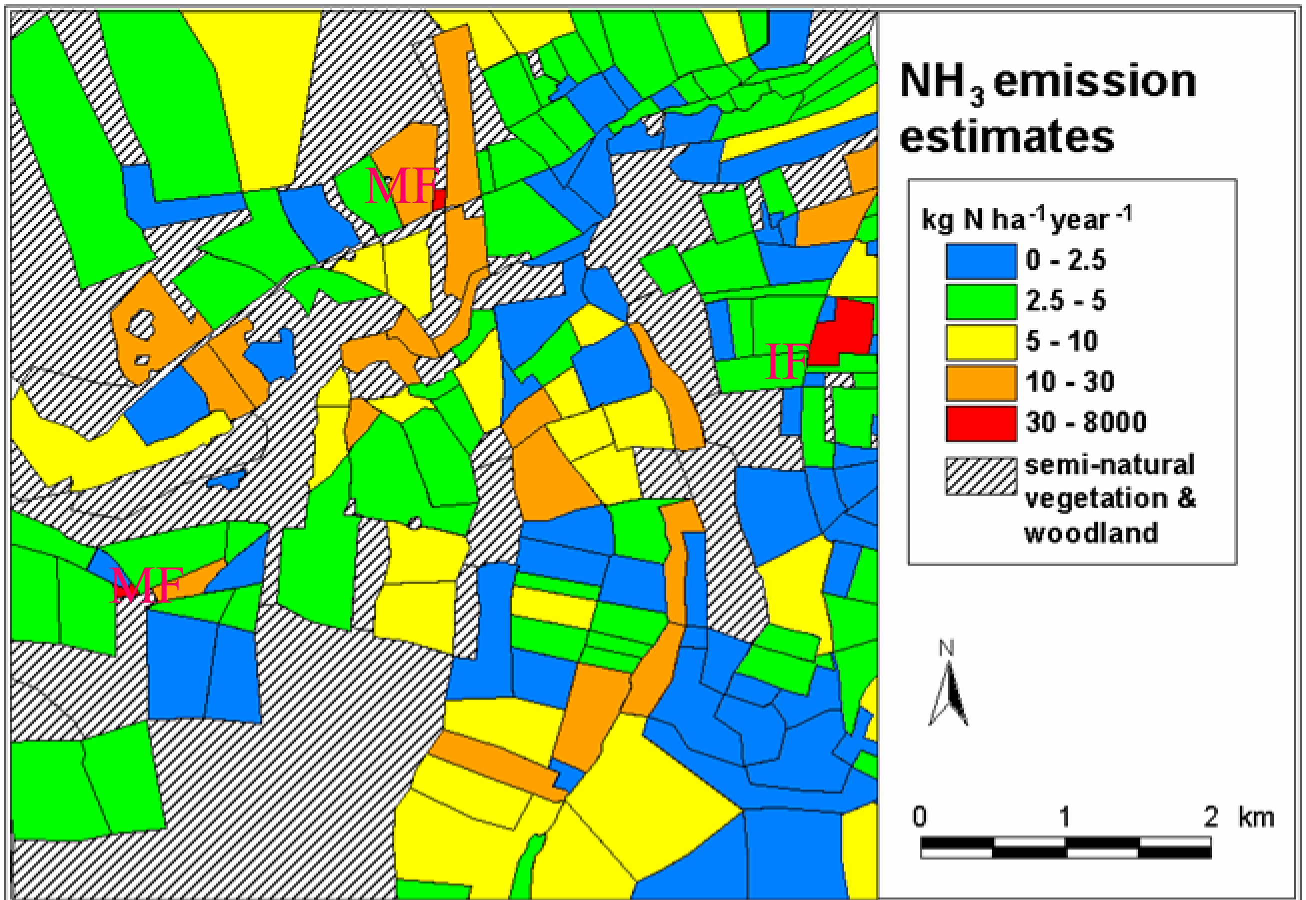
Comparison with models

- Comparing like with like – point vs. area
- Need to estimate area deposition from monitoring data
- Use models for receptor-specific estimates
- Local vs. regional scale

Deposition Monitoring Summary

- Identify purpose – why? what? where?
- Identify temporal resolution required
- Decide on precision acceptable
- Identify resources available – how to do it?
- Decide relationship with modelling
- Consider uncertainty analysis

Case Study: Ammonia emissions



IF: Intensive Farm
MF: Mixed Farm

Dragosits et al. (Environ. Pollution 2002)

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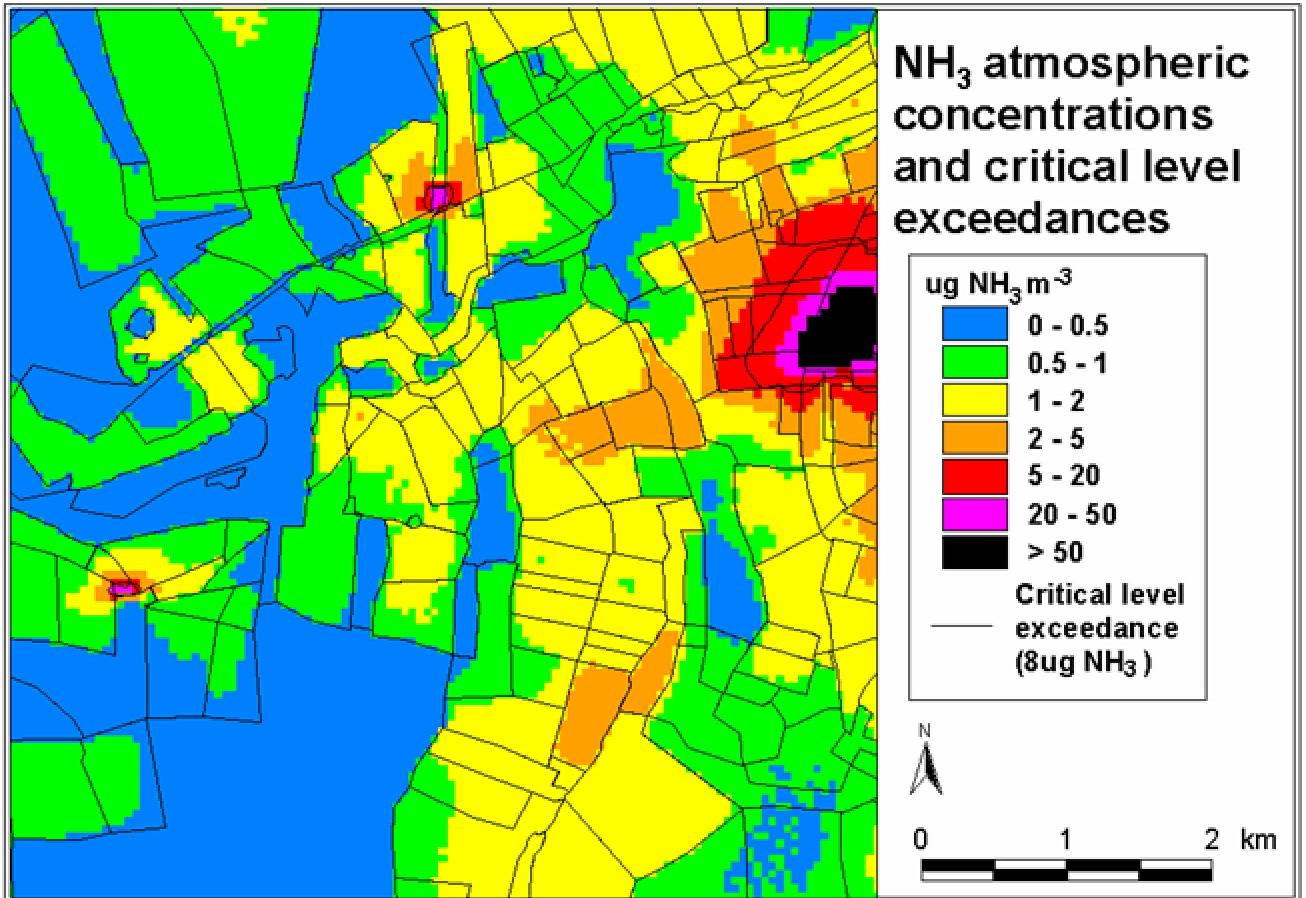
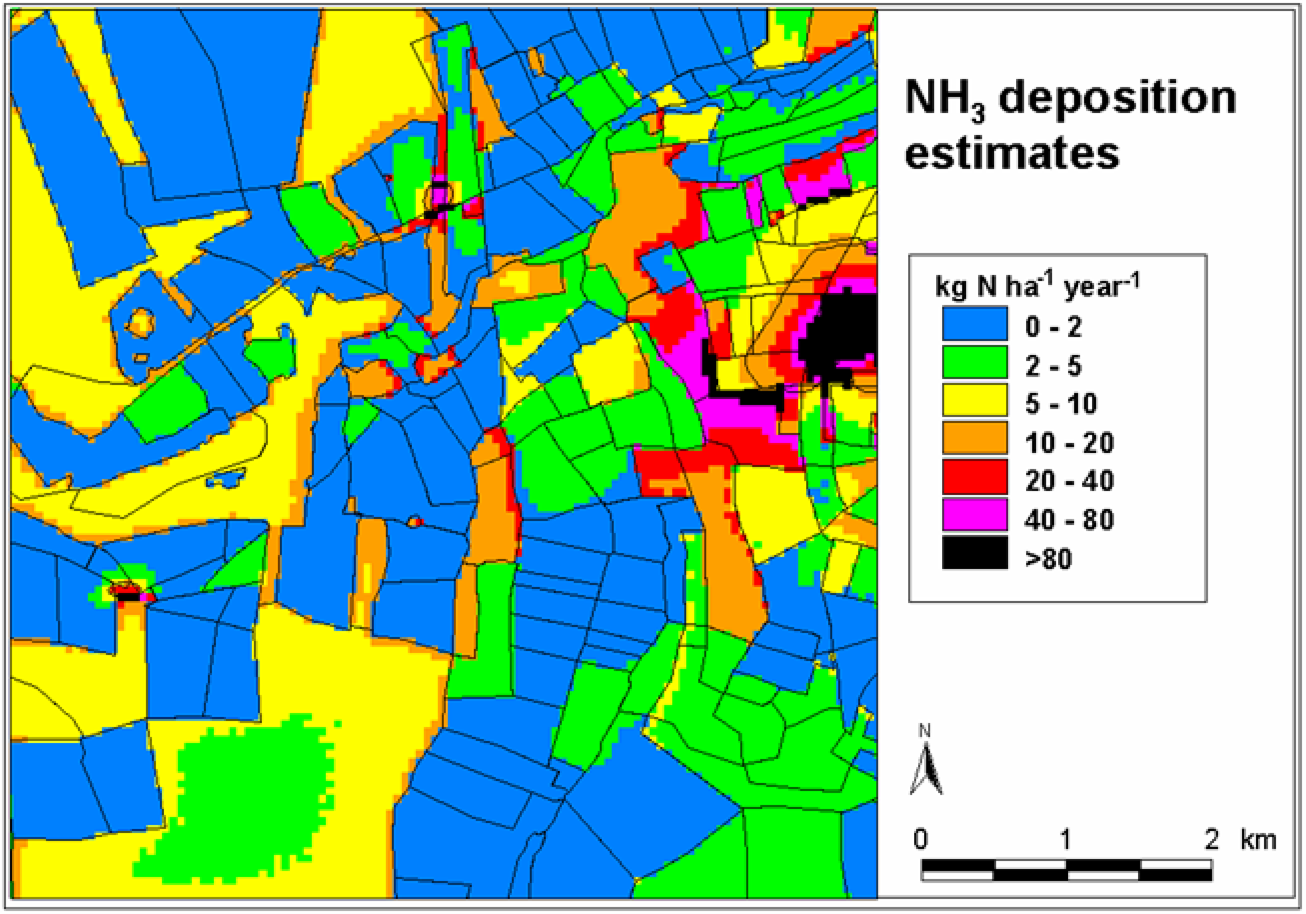
Modelled ammonia concentrations



Exceedance of the annual critical level for NH_3 is predicted up to 500 m from the intensive farm, but only in the immediate vicinity of the mixed farms

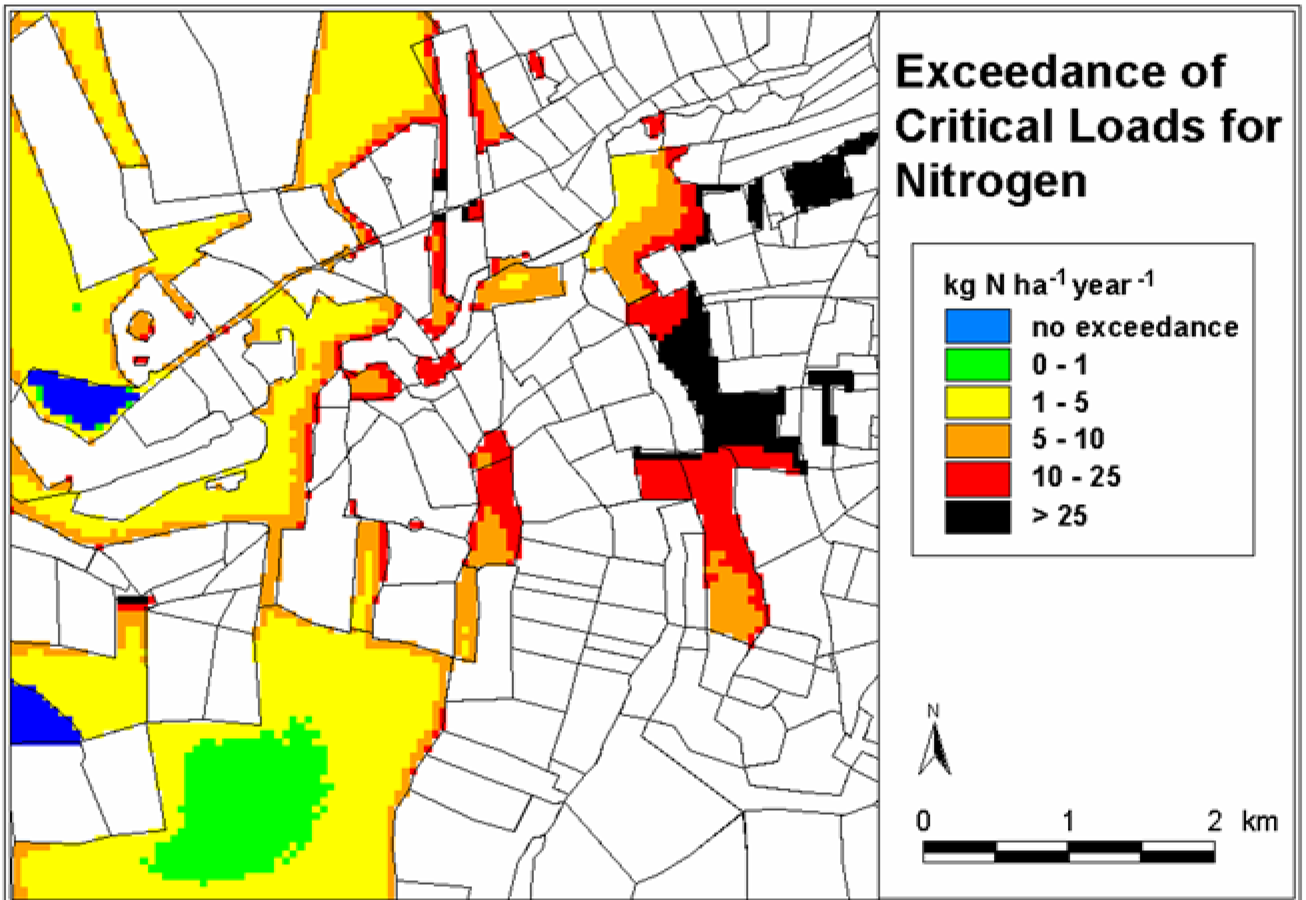
Modelled ammonia dry deposition



The largest NH_3 Deposition occurs Near the intensive Farm and at the edges Of woodland and Semi-natural land.

Deposition is less In the centre of large Semi-natural areas.

Exceedance of critical loads for nitrogen at a field scale



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