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

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Sources of ‘reactive’ N in the atmosphere

- **What to monitor**

  - Nitrogen oxides
  - Nitric and nitrous acid
  - Ammonia
    - NO, NO₂
    - HNO₃, HONO
    - NH₃
  - Nitrate and ammonium in aerosols and precipitation
    - NO₃⁻, NH₄⁺
  - Organic nitrogen
    - various...
    - PAN, urea, amines etc.
## Sources of ‘reactive’ N in the atmosphere

<table>
<thead>
<tr>
<th>What to monitor</th>
<th>Where it comes from</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen oxides</td>
<td>Combustion, soil</td>
</tr>
<tr>
<td>Nitric and nitrous acid</td>
<td>Oxidation of nitrogen oxides</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Animal wastes, senescent vegetation, 3-way catalysts</td>
</tr>
<tr>
<td>Nitrate and ammonium in aerosols and precipitation</td>
<td>Oxidation of nitrogen oxides</td>
</tr>
<tr>
<td>Organic nitrogen</td>
<td>Reaction with ammonia gas</td>
</tr>
<tr>
<td></td>
<td>Solution of nitrate and ammonium aerosols</td>
</tr>
<tr>
<td></td>
<td>Photochemical, possibly agricultural</td>
</tr>
</tbody>
</table>

**CASAC Symposium, Lake Louise, Alberta, September 2006**
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)
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.
Deposition monitoring

Wet deposition

• Cloud – is it an issue?
Deposition monitoring

Wet deposition

• ‘Bulk’ or ‘wet-only’?

**Bulk:**
- Inexpensive
- No power
- Many replicates

**Wet-only:**
- Less contamination
- Preserved samples
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

Ion balance

![Graph showing ion balance](image)

Conductivity check

![Graph showing conductivity check](image)

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Interpolation and extrapolation

generating a concentration map

more sites gives more definition (HNO$_3$ → SO$_4^{2-}$)
extra information improves structure (SO$_4^{2-}$ → NO$_2$ → NH$_3$)
Interpolation and extrapolation

Generating a deposition map

Interpolated concentration  ×  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)
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

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.

\[ \text{flux} \chi = w' \chi' \]

- \( w' \) - fluctuation in vertical wind speed
- \( \chi' \) - deviation from mean concentration
Deposition monitoring

Dry deposition

• Direct measurement

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

\[ \text{flux}_\chi = w' \chi' \]

- \( w' \) - fluctuation in vertical wind speed
- \( \chi' \) - deviation from mean concentration
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.
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.
Deposition monitoring
First Intercomparison of TDL-AS for NH$_3$ fluxes

Eddy covariance for NH$_3$ now possible – but still not easy

15:00 29/4/05 to 00:00 31/4/05
Deposition monitoring

Dry deposition

- Understanding the processes

\[ v_d = \frac{\text{flux}}{\text{concentration}} = \frac{1}{R_t} \]

\[ R_t = R_a + R_b + \left( \frac{1}{R_{c1}} + \frac{1}{R_{c2}} + \frac{1}{R_{c3}} \right)^{-1} \]

- Depend on wind speed and turbulence
- Depend on properties of the surface

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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 NH₃
Deposition monitoring

Dry deposition

- Indirect measurement – flux gradient

fetch

constant flux layer

fetch:height 100:1

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Deposition monitoring

Dry deposition

- Indirect measurement – flux gradient

\[ \text{flux}\chi = K\chi \frac{\partial\chi}{\partial z} \]

with stability correction:

\[ \text{flux}\chi = ku^* \frac{\partial\chi}{\partial \left[\ln(z - d) - \Psi_H(\zeta)\right]} \]
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
Deposition monitoring

Measured and modelled SO$_2$ flux at Auchencorth Moss over 5 days

Measured and modelled SO$_2$ flux at Auchencorth Moss over 5 days.
Deposition monitoring
Dry deposition – comparison of measurements

<table>
<thead>
<tr>
<th></th>
<th>Eddy covariance</th>
<th>Flux gradient</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equipment cost ($)</td>
<td>2-500,000</td>
<td>~ 20,000</td>
</tr>
<tr>
<td>Equipment maintenance</td>
<td>Labour intensive</td>
<td>Automated</td>
</tr>
<tr>
<td>Skills required</td>
<td>Post-doc</td>
<td>Graduate</td>
</tr>
<tr>
<td>Time resolution</td>
<td>second</td>
<td>hour</td>
</tr>
<tr>
<td>Data processing</td>
<td>Labour intensive</td>
<td>Moderate</td>
</tr>
</tbody>
</table>

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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
Deposition monitoring

Dry deposition

- Conditional time-averaged gradient (COTAG)

wind and solar powered

wind direction

samplers

wind speed
Deposition monitoring

Dry deposition

- Conditional time-averaged gradient (COTAG)

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

Dry deposition
- Inferential methods

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

$$flux = v_d \times concentration$$
Deposition monitoring

Dry deposition - Inferential methods

HNO₃ concentration

Deposition model

HNO₃ deposition

HNO₃ concentration

Depends on land use / vegetation

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Deposition monitoring

Dry deposition - Inferential methods

Measured concentration + modelled depn velocity

spatially interpolated    vegetation dependent

annual average  
monthly average  
hourly average

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 HNO₃, SO₂ and HCl

Shorter denuders 3 + 4
To remove NH₃

Aerosol filter
To remove particulate NH₄⁺, NO₃⁻, SO₄²⁻, Cl⁻, and base cations Na⁺, Ca²⁺, Mg²⁺

Air inlet

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Concentration monitoring
Example time series of monthly monitoring

Strathvaich Dam
Remote Scottish Upland Site

Sutton Bonington
SO₂ Source Region

1999 - 2005
Implementation in NitroEurope

‘Level 1’ (50 sites) continuous concentration measurements (DELTA) and measured atmospheric turbulence

‘Level 2’ (9 sites) continuous flux measurements using COTAG systems

‘Level 3’ (13 sites) 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

CEH ALPHA sampler
Fast sampling rate

1996-2001 interpolated

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

Dragosits et al. (Environ. Pollution 2002)

IF: Intensive Farm
MF: Mixed Farm
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