Techniques for measuring ammonia emissions from land applications of manure and fertiliser

Tom Misselbrook and Fiona Nicholson
Structure of presentation

- Techniques available
  - Micrometeorological
  - Enclosure

- Samplers for measuring concentration (or flux)

- Most commonly-used methodologies
  - Micrometeorological mass balance
  - Wind tunnels
  - Equilibrium concentration technique

- Conclusions
Techniques available

- Soil N balance, $^{15}$N

Micrometeorological techniques

- Mass balance
- Eddy correlation
- Gradient methods
- Backward Lagrangian stochastic model
- Equilibrium concentration technique

Enclosure techniques

- Static chambers
- Dynamic chambers

Controlled release ratio techniques
Micrometeorological techniques

Mass balance – Integrated Horizontal Flux

\[
\text{Flux from treated area} = \frac{\text{IHF}_{\text{dw}} - \text{IHF}_{\text{uw}}}{x}
\]
Micrometeorological Mass Balance (IHF) technique

Passive flux samplers mounted on a mast
Micrometeorological techniques

**Mass balance** – other methods

**Theoretical profile shape** – measure flux at 1 predetermined height ($Z_{inst}$)

**TPS Philip’s solution** – flux derived from measured concentration profile and theoretically calculated concentration profile for unit flux

**Perimeter profile method** – measure inward and outward fluxes at several heights around the perimeter of a treated circular plot
**Micrometeorological techniques**

**Eddy correlation**

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

- \( w' \) – fluctuation in vertical wind speed (sonic anemometer)
- \( \chi' \) – deviation from mean concentration (TDL)

**Relaxed eddy accumulation**

\[ \text{Flux} = b \sigma_w [\chi^+ - \chi^-] \]

- \( b \) – empirical constant
- \( \sigma_w \) – standard deviation in vertical wind
- \( \chi^+ \) – mean concentration, updraft
- \( \chi^- \) – mean concentration, downdraft

Sonic anemometer

Wet chemistry (e.g. denuder)
Micrometeorological techniques

Gradient methods

Measure concentration, wind speed and temperature at 2 or more heights

\[ \text{Flux} = K \frac{dX}{dz} \]

fetch:height 100:1
Micrometeorological techniques

Backward Lagrangian stochastic model

\[ \text{Flux} = \frac{uc}{n} \]

- \( u \) is windspeed,
- \( c \) is ammonia concentration
- \( n \) is a constant

Software commercially available

At its simplest, requires measurement of windspeed and concentration at only 1 height
Equilibrium concentration technique

\[ \text{Flux} = (C_{eq} - C_{a,z}) K_{z,a} \]
Enclosure techniques

Static chambers

Time

Concentration
Enclosure techniques

Dynamic chambers – wind tunnels

\[ \text{Flux} = V \left( C_{\text{out}} - C_{\text{in}} \right) / A \]
Controlled Release Ratio technique

\[ \text{Flux}_p = f (C_p - C_b) \]

where \( f = \frac{\text{Flux}_s}{(C_s-C_b)} \)
Samplers

- Laser/optical instruments - TDL, DOAS, FTIR
Laser/optical Instruments

Advantages:
- very sensitive
- fast response (real-time results)

Disadvantages:
- cost
- require power
Samplers

- Optical absorption samplers - TDL, DOAS, FTIR
- Absorption flasks
Absorption flasks

Advantages:
- inexpensive
- simple
- can be used for a wide concentration range

Disadvantages:
- require power
- time-averaged concentration measurements
- freezing/evaporation problems
Samplers

- Optical absorption samplers - TDL, DOAS, FTIR
- Absorption flasks
- Denuders
- Filters/badges
Filters/badges

Advantages:
- inexpensive
- simple
- no power requirement

Disadvantages:
- labour intensive
- time-averaged concentration measurements
- difficulty in estimating required exposure times
Samplers

• Optical absorption samplers - TDL, DOAS, FTIR
• Absorption flasks
• Denuders
• Filters/badges
• Passive flux samplers
Passive flux samplers – “shuttles”

Advantages:
- direct measurement of flux
- no power requirement
- simple

Disadvantages:
- cost? ($300-400 each)
- time-averaged flux measurement
Sampler inter-comparison tests

Concentration range 80 – 7,500 ug N m\(^{-3}\)
Exposure time 1 – 6 hours

- Absorption flasks – 2 in series
  - acid concentration (0.1, 0.01, 0.001M)
  - air flow rate (0.6 – 3.5 l min\(^{-1}\))
  - end type (scinttered glass, open)

- Badges
- Shuttles

angle if incidence of air flow (20\(^{\circ}\), 40\(^{\circ}\))
Sampler inter-comparison tests

Absorption flasks

✓ Mean capture in 1st flask 97%
✓ No sig. effect of acid strength
✓ No sig. effect of air flow rate
✓ No sig. effect of end type

Shuttles

✓ No sig. effect of angle of incidence
Sampler inter-comparison tests

Shuttles vs. absorption flasks

\[ y = 1.13x + 38.94 \]

\[ R^2 = 0.92 \]
Sampler inter-comparison tests

Badge vs. absorption flasks

$y = 1.77x - 583.08$

$R^2 = 0.91$
## Sampler inter-comparison tests

### Sampler repeatability

<table>
<thead>
<tr>
<th>Sampler</th>
<th>CV (%)</th>
<th>No. samplers per test</th>
<th>No. tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption flask</td>
<td>21</td>
<td>3 or 6</td>
<td>40</td>
</tr>
<tr>
<td>Shuttle</td>
<td>10</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Badge</td>
<td>14</td>
<td>4</td>
<td>6</td>
</tr>
</tbody>
</table>
## Sampler inter-comparison tests

‘Blank’ values and detection limits (ug N)

<table>
<thead>
<tr>
<th>Sampler</th>
<th>Mean ‘blank’ value</th>
<th>n</th>
<th>Detection limit</th>
<th>Maximum collected</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption flask</td>
<td>7.1</td>
<td>56</td>
<td>70</td>
<td>1130</td>
</tr>
<tr>
<td>Shuttle</td>
<td>12.7</td>
<td>18</td>
<td>48</td>
<td>770</td>
</tr>
<tr>
<td>Badge</td>
<td>1.0</td>
<td>24</td>
<td>2.5</td>
<td>260</td>
</tr>
</tbody>
</table>
Technique inter-comparisons

- Circular manure-treated plot
- 3 replicate plots
- 4 experiments (different manure types)
Technique inter-comparisons

Ammonia volatilisation rate (kg/ha/hr) on day 1

- **Slurry**
- **FYM**
- **Poultry manure**
- **Poultry manure (w etted)**

**Legend**
- Mass balance
- Micrometeorology - IHF
- Wind tunnels
- Equilibrium concentration
## Technique inter-comparisons

Coefficients of variation (%) in measured emission rates

<table>
<thead>
<tr>
<th>Technique</th>
<th>Cattle slurry</th>
<th>Cattle FYM</th>
<th>Poultry (dry)</th>
<th>Poultry (wet)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IHF</td>
<td>23</td>
<td>24</td>
<td>37</td>
<td>52</td>
</tr>
<tr>
<td>Wind tunnels</td>
<td>46</td>
<td>84</td>
<td>74</td>
<td>61</td>
</tr>
<tr>
<td>ECT *</td>
<td>30</td>
<td>37</td>
<td>39</td>
<td>36</td>
</tr>
</tbody>
</table>

* many missing data
## Choice of technique

<table>
<thead>
<tr>
<th></th>
<th>IHF</th>
<th>Wind tunnels</th>
<th>ECT</th>
</tr>
</thead>
<tbody>
<tr>
<td>type of study</td>
<td>absolute</td>
<td>comparative</td>
<td></td>
</tr>
<tr>
<td>ease of replication</td>
<td>*</td>
<td>***</td>
<td>***</td>
</tr>
<tr>
<td>land area required</td>
<td>***</td>
<td>*</td>
<td>*</td>
</tr>
<tr>
<td>capital cost</td>
<td>*</td>
<td>***</td>
<td>*</td>
</tr>
<tr>
<td>labour costs</td>
<td>*</td>
<td>**</td>
<td>***</td>
</tr>
<tr>
<td>practicality</td>
<td>*</td>
<td>*</td>
<td>**</td>
</tr>
<tr>
<td>variability</td>
<td>**</td>
<td>**</td>
<td>*</td>
</tr>
<tr>
<td>overall reliability</td>
<td>***</td>
<td>**</td>
<td>*</td>
</tr>
</tbody>
</table>

* low, ** medium, *** high
Conclusions

- Large number of techniques available
  - Overall methodology
  - Sampling concentration/flux
- CV of measurement techniques lowest for MB-IHF
- CV of measurements lower for slurries than solid manures
- Choice of technique depends on purpose and resources available
- Still room for the development of a non-intrusive small plot technique