An assessment of the applicability of ambient NH\textsubscript{3} instrumentation under field conditions

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Study aim:

Produce a series of recommendations for the best practices of the measurement of ambient NH$_3$ under field conditions.
Why recommendations required?

- Global emissions expected to increase from 65 Tg N yr\(^{-1}\) (1990) to 135 Tg N yr\(^{-1}\) (2100)\(^a\)
- Essential ambient NH\(_3\) is monitored:
  - uncertainties in the predicted emissions
  - impact on the environment and human health

\(^a\)Fowler et al. 2015 ACP.

**EMEP-EEA air pollutant emission inventory guidebook – 2013, Part A, Chapter 5, Table 3-3**

<table>
<thead>
<tr>
<th>NFR</th>
<th>SOURCE CATEGORY</th>
<th>SO2</th>
<th>NH3</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.A.1</td>
<td>Public power, cogeneration and district heating</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>1.A.2</td>
<td>Industrial combustion</td>
<td>A</td>
<td></td>
</tr>
<tr>
<td>1.A.3.b</td>
<td>Road transport</td>
<td>C</td>
<td>E</td>
</tr>
<tr>
<td>1.A.3.a</td>
<td>Other mobile sources and machinery</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>1.A.3.c</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.A.3.d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.A.3.e</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.A.4</td>
<td>Commercial, institutional and residential combustion</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>1.B</td>
<td>Extraction and distribution of fossil fuels</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Industrial processes</td>
<td>B</td>
<td>E</td>
</tr>
<tr>
<td>3</td>
<td>Solvent use</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Agriculture activities</td>
<td>D</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Waste treatment</td>
<td>B</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Disposal activities</td>
<td>C</td>
<td>E</td>
</tr>
<tr>
<td>-</td>
<td>Nature</td>
<td>D</td>
<td>E</td>
</tr>
</tbody>
</table>

D: 100 to 300 %
E: order of magnitude
Why recommendations required?

- Both in the European Monitoring and Evaluation Program (EMEP) and the US EPA:
  - Reference methods written in 1996 and 1999, respectively.
  - Methods are labour intensive
  - Requires specialist knowledge

- Great advancements in technology in the last 20 years

- Now a number of commercial instruments available measuring to ppt range and no longer (in theory) require specialised operators
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Metrology for NH$_3$ in ambient air

- 1$^{\text{st}}$ June 2014: metrology for NH$_3$ in ambient air (MetNH$_3$) project started

- Project aim:

  Developing metrological traceability for the measurement of NH$_3$ in air from primary gas mixtures and instrumental standards to field application
Field site description
Field site description
Instrumentation
Instrumentation
Instrumentation
Field site Description: Layout

Key:
- Mast/mast base (black-available, red in use)
- 2 x 240V sockets (13 Amp)
- Conduit for cables from/to cabin
- 2 commando sockets (240 V, 16 Amp)
- Temporary fencing
- Mini DOAS reflectors
- Pump box
- Passive NH₃ samplers

Note: Not to scale

Approximate sampling height 1.7 m

North field

South field
Field site Description: Layout

Key:
- Mast/mast base (black-available, red in use)
- 2 x 240V sockets (13 Amp)
- Conduit for cables from/to cabin
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- Pump box
- Passive NH₃ samplers

Mean wind speed = 1.81 m s⁻¹
Field site Description: Layout

Approximate sampling height 1.7 m

Key:
- Mast/mast base (black-available, red in use)
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Note: Not to scale
## Summary of setup

<table>
<thead>
<tr>
<th>Location</th>
<th>Instrument</th>
<th>Total Inlet Length (m)</th>
<th>Flowrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scaffold 1</td>
<td>Mini DOAS #1</td>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
<tr>
<td></td>
<td>Mini DOAS #2</td>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
<tr>
<td></td>
<td>Mini DOAS #3</td>
<td>Not applicable</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Scaffold 2</td>
<td>AiRRmonia #1</td>
<td>0.05</td>
<td>1.0</td>
</tr>
<tr>
<td>Tow van</td>
<td>QCL (Aerodyne)</td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>AP2E</td>
<td>4.69</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>AiRRmonia #2</td>
<td>6.40</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>Picarro #1</td>
<td>4.88</td>
<td>0.8</td>
</tr>
<tr>
<td></td>
<td>Low cost sensors</td>
<td>3.7</td>
<td>2.0</td>
</tr>
<tr>
<td>Green mobile laboratory</td>
<td>*LGR#1 (Economical Ammonia Analyser)</td>
<td>2.0</td>
<td>0.25</td>
</tr>
<tr>
<td></td>
<td>*LGR#2 (Economical Ammonia Analyser)</td>
<td>1.45</td>
<td>2.30</td>
</tr>
<tr>
<td></td>
<td>*Picarro#2</td>
<td>2.15</td>
<td>1.35</td>
</tr>
<tr>
<td></td>
<td>*Tiger optics</td>
<td>2.64</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>*LSE monitors</td>
<td>1.12</td>
<td>0.10</td>
</tr>
<tr>
<td>Posts</td>
<td>MARGA</td>
<td>8.46</td>
<td>16.7</td>
</tr>
<tr>
<td></td>
<td>Alphas</td>
<td>Not applicable</td>
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* Instruments which are on the common manifold (Inlet to common manifold length 3.5m, with a flowrate of ~45L/min)
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<td>1.35</td>
</tr>
<tr>
<td></td>
<td>*Undisclosed instrument</td>
<td>2.64</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
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<td>1.12</td>
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<td>n/a</td>
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* Instruments which are on the common manifold (Inlet to common manifold length 3.5m, with a flowrate of ~45L/min)
23 August 2016 both fields fertilised with 35 kg N h\(^{-1}\) of urea (pellets)
Time series results

Rainfall (mm)

Individual inlets

NH₃ (ppb)

Manifold

Scaffolding

Date/time (GMT)

23/08/2016

25/08/2016

27/08/2016

Airrmonia #2 (5 min)
Aerodyne QCL (1 s)
MARGA (1 hour)
AP2E (1 min)
Picarro #1 (1 min)

LSE (1 min)
LGR #1 (1 s)
LGR #2 (1 s)
Tiger Optics (1 min)
Picarro #2 (1 min)

Airrmonia #1 (1 min)
DOAS #1 (1 min)
DOAS #2 (1 min)
DOAS #3 (1 min)
Hourly data

- MARGA
- Airmonia #1
- Airmonia #2
- Picarro #1
- Picarro #2
- Mini DCAS #1
- Mini DCAS #2
- Mini DCAS #3
- *LSE
- *LGR #1
- *LGR #2
- OCL
- Undisclosed instrument
- AP$_3$E

- ALPHAs (exposed 22/08/16 to 29/08/16)

* instrument was on the common manifold
Instruments vs Ensemble average (23/08 - 28/08)

Mini DOAS

\[ y = 0.92x - 0.03 \]

\[ R^2 = 0.98 \]

Wet chemistry

Individual inlets
Instruments vs Ensemble average (23/08 - 28/08)

Mini DOAS

Manifold

Wet chemistry

Individual inlets
Instruments vs Ensemble average (23/08 - 28/08)

- Mini DOAS
- Manifold
- Wet chemistry
- Individual inlets

[Graphs showing data correlation between different measurement methods and ensemble average.]
Instruments vs Ensemble average (23/08 - 28/08)

- Mini DOAS
- Manifold
- Wet chemistry
- Individual inlets
Instruments vs Ensemble average (23/08 - 28/08)

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Field calibrations

• 2 dynamic and 1 static calibration systems present
• METAS traceable reference gas generator (REGAS) used to check concentrations before and after intercomparison for low flow instruments (Picarro, LGR, LSE, Tiger Optics)
• NPL static calibrator used for high flow instruments and mini DOAS
• Results still being assessed
• MetNH₃ reports will assess operational requirements and challenges for practical use of such systems in the field
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Next steps:

• Assessment on the applicability of calibration system in the field
• Evaluate the performance of instruments with the dynamic calibration system
• Produce a final series of recommendations with regards to the optimum operation for NH$_3$ instrumentation
• write measurement guideline documents for AQ networks, EMEP and WMO-GAW
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Conclusions:

• Though technology has advanced users need some understanding in order to choose the right instrument for their application.

• Low-flow instruments either need minimal inlet or a high-flow inlet with sub-sampling off for operation.

• Simple measurement guidelines are needed.

• Recommended that there should be a world centre for ammonia measurements for WMO-GAW.

• When measurements are undertaken quality control procedures need to be implemented.
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Acknowledgements:

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Stakeholders

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Centre for Ecology & Hydrology
Natural Environment Research Council

MetNH₃

NERC
Science of the Environment