N fluxes from the agricultural sector

Elizabeth Pattey
Ray Desjardins, Jennifer Murphy, Doug MacDonald

GLOBAL ATMOSPHERE WATCH INT’L WORKSHOP ON NITROGEN CYCLE
13-14 April 2016, University of York, UK
Global Population trends (1860-2000) and reactive N (Nr) creation

N Cascade: sequential effects of a N atom on various reservoirs after its conversion to Nr

Conceptual diagram of the components of an AQ modelling system

Seigneur and Moran (2004)
Scale of Measurements: from agr. inventories to gridded data

Hierarchy

- Ecozone
  - Ecoprovence
    - Ecoregion
      - EcoDistrict → Soil Landscape (SL) Polygon

- Emission estimates are scaled to the SL polygon level
Conceptual diagram of the components of an AQ modelling system

Temporal resolution

Seigneur and Moran (2004)
Flux measuring tools for a wide range of scales

Representative Area of Measurements

- 1 m²
- 1 Hectare
- 1 km²
- 10 km²

Representative Time of Measurement

- 1 hour
- 1 Day
- 1 Month
- 1 Year

- Chamber / Wind Tunnel
- Open-path Laser bLS
- Closed-path Laser
- Aircraft EC & REA
- Flux Tower EC, FG, REA
- Tall Tower/ Flask Atmospheric Inversion
Micrometeorological techniques to measure N₂O Fluxes from cultivated fields

- Eddy Covariance

\[ F_S = \bar{\rho}_a \frac{M_S}{M_a} (w' s') \]

- Relaxed Eddy Accumulation

\[ F_S = A \sigma_w \frac{M_S}{M_a} \bar{\rho}_a (\bar{s}^+ - \bar{s}^-) \]

- Flux Gradient

\[ F_S = -K \frac{M_S}{M_a} \rho_a \frac{\Delta s}{\Delta z} \]

\[ = \frac{-u_* k (M_S/M_a) \rho_a (s_2 - s_1)}{\ln((z_2 - d)/(z_1 - d)) - \psi_{h_2} + \psi_{h_1}} \]

Natural vs anthropogenic N$_2$O emissions

2005

Global maps of direct N$_2$O emissions from Agricultural soils in 2008

Agriculture and N₂O emissions

Agriculture:
- 60% (2.8 Gt CO₂e) of anthropogenic N₂O emissions globally and 70-75% in Canada and US
- 92% of N₂O emissions attributed to N management

(Davidson et al., 2014)
Sources of N₂O from agricultural soil and driving factors

- N₂O emissions following application of synthetic/manure fertilizers mainly caused by denitrification and nitrification

- Distal factors as climate influence local environmental conditions and the proximal factors on N₂O emissions

The vast majority of $\text{N}_2\text{O}$ Flux measurements are made using non-flow through, non-steady state chambers coupled to ECD Gas Chromatography.

$$F_{\text{N}_2\text{O}} = \frac{d\text{N}_2\text{O}}{dt} \frac{V}{A} \frac{M_w}{M_v}$$

Experimental design for comparing management practices and environmental conditions
However, $\text{N}_2\text{O}$ Fluxes are highly episodic in cultivated fields, so chamber low sampling frequency affects cumulative $\text{N}_2\text{O}$ fluxes.

However, N\textsubscript{2}O Fluxes are highly episodic and heterogeneous in cultivated fields and intense grazed area (e.g., NZ).

Only TDL flux data collected between 1100 and 1300 h during days of chamber sampling were compared with the chamber flux data (40 chambers deployed).

Measuring N$_2$O Fluxes from Field using Fast-response Tunable Diode Laser Flux-Gradient technique

- Performed over agricultural fields (in the inertial sublayer)
- Concentration is measured sequentially at a fast-rate, typically 5-10 s, with data omitted during gradient valve switching (avoid fringing impact on flux measurement)
- N$_2$O fluxes need to be measured during rainy conditions and spring thaw in snowy regions, where the technique is quite robust
- Easier to monitor several sites without introducing instrumental bias

Flux Towers are the only suitable measuring approach ...

Obtaining Nr flux estimates at regional and national scales

Process-based models are used:
- Bottom up approach
- Verification of potential BMPs over space and time
However, $\text{N}_2\text{O}$ Fluxes are highly episodic in cultivated fields.

Non-linear increase of $\text{N}_2\text{O}$ emissions with fertilizer application rate.

Field-scale $N_2O$ flux measurements are continuously used to verify and improve process-based models such as:

- Ecosys
- DNDC
- Daycent
- STICS

Through the Global Research Alliance (GRA) on agricultural GHG, more than 20 international modelling teams are part of a blind test to verify the models, with incremental data provided. We are the only data site with sustained snow cover in winter.

Verified models that respond well to climate variations, could then be used to evaluated the robustness of beneficial management practices over multiple years (i.e., climatic time series).
Aircraft-Based GHG Flux Measurements

Desjardins et al. (2000)

- Laser Altimeter
- Side-looking video camera
- Satellite simulator
- Gas analyzers (CO₂, H₂O)
- Duct pressure, temperature sensors
- Radio altimeter
- Accelarometers
- Rate gyros
- Dat recorder
- REA system
- Intake
- Litton 90 inertial reference system
- Global positioning system antenna
- Console, keyboard & navigation system controls
- Dew point sensor
- Rosemount 858 (α, β, airspeed, altitude)
- Video camera
- Altitude gyro
- Radio altimeter

Desjardins et al. (2000)
TDL configuration for analyzing samples collected using the Relaxed Eddy Accumulation technique


\[ \mu = -0.8\text{pptv} \quad \sigma = 8.9\text{pptv} \]
Laird Study Township: Land Use

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>P/W</th>
<th>G</th>
<th>G</th>
<th>G</th>
<th>G</th>
<th>P</th>
<th>G</th>
<th>G</th>
<th>G</th>
<th>C</th>
<th>P/G</th>
<th>G</th>
<th>G</th>
<th>G</th>
</tr>
</thead>
<tbody>
<tr>
<td>31</td>
<td>G</td>
<td>G/C</td>
<td>G</td>
<td>C</td>
<td>P/G</td>
<td>C</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>P</td>
<td>C/G</td>
<td>P/G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>32</td>
<td>G</td>
<td>G/C</td>
<td>G</td>
<td>G</td>
<td>P/G</td>
<td>C</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>33</td>
<td>G</td>
<td>G/C</td>
<td>G</td>
<td>G</td>
<td>P/G</td>
<td>C</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>34</td>
<td>G</td>
<td>G/C</td>
<td>G</td>
<td>G</td>
<td>P/G</td>
<td>C</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>35</td>
<td>G</td>
<td>G/C</td>
<td>G</td>
<td>G</td>
<td>P/G</td>
<td>C</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
<tr>
<td>36</td>
<td>G</td>
<td>G/C</td>
<td>G</td>
<td>G</td>
<td>P/G</td>
<td>C</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
<td>G</td>
</tr>
</tbody>
</table>

Township 43, Range 4, West of the Third Meridian

- C Canola
- G Grain
- P Pulse
- F Forage/Pasture

Sampled Quarter-section

Pattey et al. (2007); Pennock et al., (2005)
Spring thaw $\text{N}_2\text{O}$ emissions in Western Canada – DNDC Model

![Graph showing $\text{N}_2\text{O}$ flux (mg N m$^{-2}$ d$^{-1}$) over calendar days. The graph includes data from Laird and DNDC models, with Chamber data represented by squares.](image)
Ammonia (NH$_3$) is a reactive and toxic gas

The Primary source of NH$_3$ emissions is agriculture

Ammonia is released mainly during naturally occurring processes, such as the breakdown of excreted urea (cattle and pigs) or uric acid (poultry).

Ammonia emissions also come from N fertilizers containing urea or ammonium.

Very high NH$_3$ emissions to the atmosphere occur in regions with concentrated livestock production.

Global annual emissions ~ 18000 kt yr$^{-1}$

mostly coming from fertilizer application in (sub-)tropical countries

NEMA: National Emission Model for Ammonia  
TAN: total ammoniacal N in manure  
Velthof et al. (2012). A model for inventory of ammonia emissions from agriculture in the Netherlands
National emission inventory (NEI) agricultural emissions in 2011 (kt yr⁻¹)

From the US National Emission Inventory

<table>
<thead>
<tr>
<th>Sector</th>
<th>NH₃</th>
<th>NOₓ</th>
<th>PM₁₀</th>
<th>PM₂.₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crops &amp; Livestock Dust</td>
<td>4502</td>
<td>897</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fertilizer Application</td>
<td>1183</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Livestock Waste</td>
<td>2344</td>
<td>0.13</td>
<td>0.34</td>
<td>0.19</td>
</tr>
<tr>
<td>Agricultural Field Burning</td>
<td>3.5</td>
<td>43.2</td>
<td>142.3</td>
<td>95.4</td>
</tr>
</tbody>
</table>


From Env Canada Inventory

<table>
<thead>
<tr>
<th>Sector</th>
<th>NH₃</th>
<th>NOₓ</th>
<th>PM₁₀</th>
<th>PM₂.₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crop Production</td>
<td>1544</td>
<td>381</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fertilizer Application</td>
<td>124</td>
<td>6.2</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>Animals Production</td>
<td>303</td>
<td>9.7</td>
<td>2.0</td>
<td></td>
</tr>
<tr>
<td>Agriculture - Fuel Combustion</td>
<td>0.1</td>
<td>3.9</td>
<td>0.5</td>
<td>0.3</td>
</tr>
</tbody>
</table>

## Ammonia Emissions from agriculture by countries (Eurostats, 1990 -2013)

<table>
<thead>
<tr>
<th>Country</th>
<th>Emissions 1990 (1 000 tonnes)</th>
<th>Emissions 2013 (1 000 tonnes)</th>
<th>Change, 1990-2013</th>
<th>Share of EU-28 emissions, 2013 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EU-28</td>
<td>5 028.4</td>
<td>3 591.3</td>
<td>-28.6</td>
<td>100.0</td>
</tr>
<tr>
<td>Belgium</td>
<td>108.9</td>
<td>56.0</td>
<td>-48.8</td>
<td>1.0</td>
</tr>
<tr>
<td>Bulgaria</td>
<td>118.0</td>
<td>27.1</td>
<td>-75.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Czech Republic</td>
<td>156.0</td>
<td>66.1</td>
<td>-57.7</td>
<td>1.8</td>
</tr>
<tr>
<td>Denmark</td>
<td>123.7</td>
<td>70.5</td>
<td>-43.0</td>
<td>2.0</td>
</tr>
<tr>
<td>Germany</td>
<td>760.8</td>
<td>633.3</td>
<td>-15.8</td>
<td>17.6</td>
</tr>
<tr>
<td>Estonia</td>
<td>25.0</td>
<td>10.6</td>
<td>-57.7</td>
<td>0.3</td>
</tr>
<tr>
<td>Ireland</td>
<td>108.0</td>
<td>106.3</td>
<td>-1.5</td>
<td>3.0</td>
</tr>
<tr>
<td>Greece</td>
<td>84.5</td>
<td>59.0</td>
<td>-30.2</td>
<td>1.6</td>
</tr>
<tr>
<td>Spain</td>
<td>316.2</td>
<td>351.0</td>
<td>11.0</td>
<td>9.8</td>
</tr>
<tr>
<td>France</td>
<td>729.0</td>
<td>700.6</td>
<td>-3.9</td>
<td>19.5</td>
</tr>
<tr>
<td>Croatia</td>
<td>50.3</td>
<td>29.4</td>
<td>-41.6</td>
<td>0.8</td>
</tr>
<tr>
<td>Italy</td>
<td>461.3</td>
<td>385.7</td>
<td>-16.4</td>
<td>10.7</td>
</tr>
<tr>
<td>Cyprus</td>
<td>5.1</td>
<td>4.4</td>
<td>-14.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Latvia</td>
<td>38.1</td>
<td>11.3</td>
<td>-70.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Lithuania</td>
<td>96.9</td>
<td>37.6</td>
<td>-61.3</td>
<td>1.0</td>
</tr>
<tr>
<td>Luxembourg</td>
<td>4.9</td>
<td>4.3</td>
<td>-11.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Hungary</td>
<td>140.8</td>
<td>77.2</td>
<td>-47.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Malta</td>
<td>1.9</td>
<td>1.5</td>
<td>-20.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Netherlands</td>
<td>351.3</td>
<td>113.8</td>
<td>-67.6</td>
<td>3.2</td>
</tr>
<tr>
<td>Austria</td>
<td>63.6</td>
<td>62.0</td>
<td>-2.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Poland</td>
<td>490.3</td>
<td>258.5</td>
<td>-47.3</td>
<td>7.2</td>
</tr>
<tr>
<td>Portugal</td>
<td>56.1</td>
<td>44.0</td>
<td>-21.7</td>
<td>1.2</td>
</tr>
<tr>
<td>Romania</td>
<td>262.4</td>
<td>139.1</td>
<td>-47.0</td>
<td>3.9</td>
</tr>
<tr>
<td>Slovenia</td>
<td>216</td>
<td>16.9</td>
<td>-21.8</td>
<td>0.5</td>
</tr>
<tr>
<td>Slovakia</td>
<td>63.1</td>
<td>24.4</td>
<td>-61.3</td>
<td>0.7</td>
</tr>
<tr>
<td>Finland</td>
<td>35.1</td>
<td>33.8</td>
<td>-3.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Sweden</td>
<td>49.0</td>
<td>45.2</td>
<td>-7.6</td>
<td>1.3</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>307.8</td>
<td>221.9</td>
<td>-27.9</td>
<td>6.2</td>
</tr>
<tr>
<td>Iceland</td>
<td>5.8</td>
<td>5.3</td>
<td>-2.6</td>
<td>0.1</td>
</tr>
<tr>
<td>Liechtenstein</td>
<td>0.2</td>
<td>0.2</td>
<td>-1.7</td>
<td>0.0</td>
</tr>
<tr>
<td>Norway</td>
<td>23.4</td>
<td>25.1</td>
<td>7.4</td>
<td>0.7</td>
</tr>
<tr>
<td>Switzerland</td>
<td>69.5</td>
<td>57.3</td>
<td>-17.2</td>
<td>1.6</td>
</tr>
<tr>
<td>Turkey</td>
<td>502.5</td>
<td>1 060.8</td>
<td>111.1</td>
<td>29.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Year</th>
<th>North-Am</th>
<th>US</th>
<th>Canada</th>
<th>Mexico</th>
</tr>
</thead>
<tbody>
<tr>
<td>1990</td>
<td>4921</td>
<td>3421</td>
<td>468</td>
<td>1032</td>
</tr>
<tr>
<td>1999</td>
<td>4594</td>
<td>3551</td>
<td></td>
<td>616</td>
</tr>
<tr>
<td>2011</td>
<td>427</td>
<td></td>
<td></td>
<td>616</td>
</tr>
</tbody>
</table>

Slurry application rate = 58 kg N ha\(^{-1}\)

\(\text{NH}_3\) emission = 7% N applied

\(\text{NH}_3\) short-range deposition = 2% N applied
Ammonia Emission: TDL vs Denuder tubes

Slurry application rate = 77 kg N ha\(^{-1}\)
NH\(_3\) emission = 16% N applied
How to measure ammonia (NH$_3$) fluxes with eddy covariance (EC)

**Challenges:**
- EC requires fast NH$_3$ measurements (10 Hz) → $c'_{NH_3}$
- NH$_3$ is a “sticky” molecule and adsorption /desorption effects have to be considered.
- Bulky instrumentation used for NH$_3$ measurements may significantly influence the wind field of the sonic anemometer.
- Especially for measurements of bi-directional exchange, where the net flux is often close to zero, the determination of accurate NH$_3$ fluxes is a major challenge.

$F_{NH_3} = w' c'_{NH_3}$

Quantum Cascade Tunable Laser Infrared Absorption Spectroscopy (QC-TILDAS)

Jennifer Murphy’s group, University of Toronto
**Time response: influence of inlet length**

Jennifer Murphy’s group, University of Toronto

**NH₃**

Zero air

Double exponential fit function:

\[ y = y_0 + A_1 \exp\left(\frac{-(t - t_0)}{\tau_1}\right) + A_2 \exp\left(\frac{-(t - t_0)}{\tau_2}\right) \]

Different inlet tube lengths:
- 120 ft
- 40 ft
- 6 ft

Exchange of air volume
Tube wall effects
Time response: influence of inlet length

Jennifer Murphy’s group, University of Toronto

\[ \tau_1 = 0.87 \, s \]
\[ \tau_2 = 15.7 \, s \]

\[ \tau_1 = 0.41 \, s \]
\[ \tau_2 = 13.5 \, s \]

\[ \tau_1 = 0.26 \, s \]
\[ \tau_2 = 5.4 \, s \]
Time response (cont.): influence of inlet contamination

Jennifer Murphy’s group, University of Toronto

NH₃

zero air

time response:

\[ \tau_1 = 2.57 \, \text{s} \]
\[ \tau_2 = 43.0 \, \text{s} \]

\[ \tau_1 = 0.41 \, \text{s} \]
\[ \tau_2 = 13.5 \, \text{s} \]
Conceptual diagram of the components of an AQ modelling system

- Population, Econometric, Land-Use, Speciation, and Temporal Data
- Geophysical Data
- Emission Inventories (Canada, U.S., Mexico)
- Meteorological Observations

Emissions Processing System
- point
- area
- mobile
- biogenics

Prognostic Meteorological Model

Regional Chemical Transport Model

Pollutant Concentration & Deposition Fields (gases, aerosols)

Seigneur and Moran (2004)
What could be done for having the bottom-up research to better contribute to the AQ modelling?

- **Reduce the need for disaggregating over space and time**
- Progressing from Tier 1 emissions towards Tier 3 (using verified models)
- Using more precise inventories (e.g. milk quota to know the animal units per animal housing) access to crop insurance information, EO (e.g., Sentinel) for crop identification, crop area, management practices (directly or derived from assimilation), and vigor, etc.
- Increase the number of experiments in agriculture that perform simultaneously the measurements of NH₃ and N₂O fluxes at the production unit scale (field, animal feedlots, etc.) to evaluate beneficial management practices, knowing that trade-off issues exist.
- Measure at the watershed and regional scale, NH₃ and N₂O fluxes using aircraft / tall towers, to verify model/inventories estimates and derive indirect N₂O emissions.
- Improve and verify process-based models (e.g., soil-crop, environmental) with high temporal resolution
- Improve landscape models wrt N cycle (including hydrology, topography, land use, etc.)
Challenges and Recommendations

• The bottom up N\textsubscript{2}O, ammonia emissions are marginally measured at the field, animal housing and waste storage, farm scales, which are the critical scales for identifying mitigation practices in agriculture.

• Measuring N\textsubscript{2}O, ammonia emissions from agricultural fields and grasslands using flux towers is challenging, with specific issues for each species.

• Instrumentation is costly and highly qualified personal is required. However, the requirements vary and can sometimes be downgraded.

• Both WMO commissions should play an active role for encouraging the emergence of regional multidisciplinary teams made of atmospheric chemists, micrometeorologists, process-based and atmospheric modellers.

• These regional multidisciplinary teams will be essential to overcome measurements challenges, to better design experimentation to fill knowledge gaps in atmospheric reactive N fluxes and the fate of secondary PM, specific to various regions.
Thank you!

For more information: Elizabeth.Pattey@canada.ca
The Gothenburg Protocol of the UN Convention on Long-range Transboundary Air Pollution (UNECE, 1999) &

The EU National Emission Ceiling Directive (European Commission, 2001)

have set limits to NH$_3$ emissions.

Therefore countries have to report their NH$_3$ emissions to the UNECE and/or the European Commission.

Moreover, countries have to report their NH$_3$ emissions as a basis for their N$_2$O emission calculation to the UNFCCC.

A guidebook has been made for inventories of emissions of air pollutants, including NH$_3$ (EMEP/EEA, 2009).

Refinement of the projections of NH$_3$ emission are needed to find effective options to mitigate NH$_3$ emissions.