Nitrous Oxide Monitoring in Agriculture

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Outline

- Introduction
  - Nitrous oxide and global warming
  - Nitrous oxide and agriculture
- How do soils generate N$_2$O?
- What factors affect N$_2$O production in soils?
- How can we monitor N$_2$O fluxes?
  - Direct methods
    - Chambers (manual, automatic)
    - Tunable diode laser absorption spectroscopy
    - Isotopic (15N)
  - Indirect methods
    - Accounting (e.g., IPCC)
    - Models (e.g., DNDC, DayCent, EPIC)
- Summary
First, a reality check from the facts synthesized in the 4th Assessment Report of IPCC, WG I, Ch. 2

- Human activities result in emissions of four principal greenhouse gases: CO₂, CH₄, N₂O and the halocarbons (a group of gases F₁, C₁ and Br).
- Atmospheric concentrations of long-lived greenhouse gases have been increasing over the last 2,000 years, especially since 1750 – the beginning of the industrial era.
- Nitrous oxide is also emitted by human activities such as fertilizer use and fossil fuel burning. Natural processes in soils and the oceans also release N₂O.

<table>
<thead>
<tr>
<th>Concentrations and Δ (ppm)</th>
<th>Radiative Forcing</th>
</tr>
</thead>
<tbody>
<tr>
<td>2005</td>
<td>Δ since 1998</td>
</tr>
<tr>
<td>CO₂</td>
<td>379</td>
</tr>
<tr>
<td>CH₄</td>
<td>1.77</td>
</tr>
<tr>
<td>N₂O</td>
<td>0.319</td>
</tr>
</tbody>
</table>

Nitrous oxide and agriculture...
Further synthesis from IPCC, WG III, Ch. 8

- Agricultural lands (cropland, grasslands and permanent crops) occupy about 40-50% of the Earth’s land surface (13.4 Bha).
- Agricultural activities resulted in emissions of 5.1-6.1 GtCO₂-eq yr⁻¹ in 2005 (10-12% of total global anthropogenic emissions of greenhouse gases):
  - CH₄ contributes 3.3 GtCO₂-eq yr⁻¹ (50% of total)
  - N₂O contributes 2.8 GtCO₂-eq yr⁻¹ (60% of total)
  - CO₂ contributes 0.04 GtCO₂-eq yr⁻¹ (~0% of total)

Aerial views of managed landscapes
The N cycle is rather complex and humans have exerted a great influence on it

- The atmosphere is a major repository of nitrogen (N₂)
- Nitrogen accumulated in soils over geologic times due to a small imbalance between biological N fixation (gain) and denitrification (loss)
- Humans have altered the N cycle by
  - Industrial fixation of nitrogenous fertilizers
  - Manipulation of domestic animals, crop residues, and harvested products

But, what is a “greenhouse gas” anyway?

- Nitrogen, O₂, and Ar make up for 99% of the atmosphere but are not greenhouse gases
- Water vapor, CO₂, CH₄, and N₂O are greenhouse gases
- A greenhouse gas absorbs infrared radiation because of their dipole moment
  - This dipole moment creates molecular vibration and bending and as a result the molecule absorbs infrared radiation
  - Collisions transfer energy to heat the surrounding gas

http://www.ucar.edu/learn/1_3_1.htm

http://ohioline.osu.edu/aex-fact/0463.html
And why is N$_2$O such as potent greenhouse gas? Two definitions and a formula

- Radiative Forcing: Change in net irradiance (W m$^{-2}$) at the tropopause after allowing stratospheric temperatures to re-adjust to radiative equilibrium, but with surface and tropospheric temperatures held at their unperturbed values
  - A positive value warms the system while a negative value cools it

- Global Warming Potential (GWP): Cumulative radiative forcing between the present and some chosen later time “horizon” caused by a unit mass of gas emitted now, expressed relative to CO$_2$

$$GWP_{N_2O} = \frac{N_2O(Wm^{-2}g^{-1}(100y)^{-1}}{CO_2(Wm^{-2}g^{-1}(100y)^{-1}}$$

- Nitrous oxide has a long lifetime in the atmosphere: 114 years
- The GWP for N$_2$O varies according to the time considered:
  - For 20 years: 310 gCO$_2$ (gN$_2$O)$^{-1}$
  - For 100 years: 298 gCO$_2$ (gN$_2$O)$^{-1}$

But before we continue with N$_2$O monitoring, let’s remind ourselves that N$_2$O also plays a role in the destruction of the stratospheric O$_3$ layer

- The stratospheric O$_3$ layer protects life from harmful solar UV radiation

- Chlorofluorocarbons (CFCs) generate atomic chlorine, which catalyze the destruction of O$_3$

- Nitrous oxide that reaches the stratosphere undergoes photolytic reactions, which lead to destruction of O$_3$
  - N$_2$O + O(1D) $\rightarrow$ 2NO
  - N$_2$O + O(1D) $\rightarrow$ N$_2$ + O$_2$

science.hq.nasa.gov/missions/satellite_22.htm
How does N\textsubscript{2}O generate in soils?

▶ Nitrous oxide is generated in soils mainly by two processes:
  - Denitrification
    - Carried out by heterotrophic microbes under anaerobic conditions
    - NO\textsubscript{3} \rightarrow NO\textsubscript{2} \rightarrow NO \rightarrow N\textsubscript{2}O \rightarrow N\textsubscript{2}
    - Denitrification is the sum of N\textsubscript{2}O and N\textsubscript{2} loss
    - The ratio N\textsubscript{2}O/(N\textsubscript{2}O+N\textsubscript{2}) varies upon environmental conditions
  - Nitrification
    - Carried out by autotrophic microbes under aerobic conditions
    - \[ \text{NH}_4^+ \rightarrow \text{NH}_3 \rightarrow \text{NO} \rightarrow \text{NO}_2^- \rightarrow \text{NO}_3^- \]

▶ Other pathways are possible
  - Chemodenitrification
  - Anammox
  - DNRA (Dissimilatory Nitrate Reduction to Ammonium)

Monitoring N\textsubscript{2}O fluxes at regional scales

▶ Objective: monitor N\textsubscript{2}O fluxes at 6 locations in Alberta, Canada during 2 years (Summer 1993 – Spring 1995)

▶ Estimated losses of N\textsubscript{2}O varied from year to year and from site to site
  - 0.4 kg N\textsubscript{2}O-N ha\textsuperscript{-1} at Breton
  - 2.6 kg N\textsubscript{2}O-N ha\textsuperscript{-1} at Eckville

▶ Losses of N\textsubscript{2}O-N during the spring thaw accounted for as much as 70% of the annual loss

▶ Clay content explained up to 92% of the large-scale spatial variability in the annual estimates of N\textsubscript{2}O-N
Automated chambers can provide much better temporal coverage than manually-operated systems

Field scale measurements of trace gases with a TGA and micrometeorological techniques

Trace gases can be measured at field scale combining diode laser absorption spectroscopy and micrometeorological techniques

Instrumentation offers rapid sampling rates to be used with eddy correlation and flux gradient techniques


CH$_4$ (A) and N$_2$O (B) fluxes from grass and fallow soil at Elora (Ontario) in 1992

- Mostly for country or regional scale
- Three methodologies:
  - Tier 1: basic, direct \( N_2O \) emissions from managed soils estimated as:
    - \( N_2O_{ot}^N = N_2O - N_{NIRP} + N_2O - N_{OS} + N_2O - N_{HRP} \)
    - For N inputs, calculation includes fertilizer N, organic amendments, crop residues, N mineralization
  - Tier 2: more detailed emission factors and data (e.g., organic N)
  - Tier 3: modeling or measurement approaches (e.g., DNDC, DayCent)

DNDC, a biogeochemical model to simulate soil carbon dynamics and trace gases in agriculture
Li et al. (1992a,b) J. Geophys. Res. 97

- Denitrification in DNDC occurs under oxygen-deficient conditions (e.g., wet soils following rain events)
- Nitrates are converted to \( NO_2^- \) and then to \( N_2O \) and \( N_2 \)
- Nitrous oxide production and denitrification are functions of carbon decomposition, soil pH, soil water content, and soil temperature
- Li et al. (1996) produced generalized estimates of \( N_2O \) fluxes across U.S. agricultural lands

Modeling \( N_2O \) and \( N_2 \) production generated from denitrification and nitrification processes

- Daily time step process-based model developed on the basis of the Century model
- Models nitrification as a function of soil pH, soil water content, soil temperature, and soil \( NH_4^+ \) level
- \( N_2O \) formation during nitrification is a direct function of nitrification rate
- \( N_2O \) and \( N_2 \) formation during denitrification is modeled as a function of heterotrophic respiration, soil \( NO_3^- \) level, and water-filled pore space (WFPS)

KBS Long-Term Ecological Research (LTER) Site

<table>
<thead>
<tr>
<th>Ecosystem Type</th>
<th>Management Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual Crops (Corn - Soybean - Wheat)</td>
<td>High</td>
</tr>
<tr>
<td>Conventional tillage</td>
<td></td>
</tr>
<tr>
<td>No-till</td>
<td></td>
</tr>
<tr>
<td>Low-input with legume cover</td>
<td></td>
</tr>
<tr>
<td>Organic with legume cover</td>
<td></td>
</tr>
<tr>
<td>Perennial Crops</td>
<td></td>
</tr>
<tr>
<td>Alfalfa</td>
<td></td>
</tr>
<tr>
<td>Poplar trees</td>
<td></td>
</tr>
<tr>
<td>Successional Communities</td>
<td></td>
</tr>
<tr>
<td>Early successional old field</td>
<td></td>
</tr>
<tr>
<td>Mid successional old field</td>
<td></td>
</tr>
<tr>
<td>Late successional forest</td>
<td>Low</td>
</tr>
</tbody>
</table>
Full Carbon Accounting in Agroecosystems

1. Soil C Oxidation
2. Fuel
3. Nitrogen Fertilizer
4. Lime (CaCO$_3$) and Ca in Irrigation Water
5. Non-CO$_2$ Greenhouse Gases
   - N$_2$O
   - CH$_4$

Do no till cropping systems emit more N$_2$O than conventional till systems?

- No till systems are perceived to emit more N$_2$O than conventional till systems

Conclusions
- No till increased soil C
- No till improved aggregation
- N2O fluxes were higher in no till in 2 out the 10 years, but on average there was no difference
- Yields were not different

<table>
<thead>
<tr>
<th>CO$_2$ equivalent</th>
<th>Conventional till</th>
<th>No till</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil C storage</td>
<td>6</td>
<td>9.8</td>
</tr>
<tr>
<td>N$_2$O emissions</td>
<td>6.3</td>
<td>3.8</td>
</tr>
<tr>
<td>GWP (N$_2$O + CO$_2$)</td>
<td>8.3</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Global Warming Potentials
Scaling gas fluxes over space and time

Time arrow

Databases, remote observations

Experiments

10^6 m^2

10^9 m^2

10^12 m^2

Simpler models, metamodels?

Process models, landscape models

Upscaling N_2O fluxes from hillslope to field scale


- Landscape position (shoulder, backslope, footslope, and depression) affected N_2O fluxes but the pattern varied seasonally
- Upscaling N_2O fluxes by landscape position increased estimates by at least 7%, in 5 out of 6 occasions, compared to arithmetic averaging
- At one site, water-filled pore space and N rate explained >70% of the N_2O variability

Upscaling N₂O fluxes from fields (40 ha) to township scale (9200 ha)

- N₂O fluxes measured by chamber methods during the 2002 spring thaw at 12 sites in a township near Laird, Saskatchewan (Canada)
  - Canola, pea, and wheat residues
  - Cattle manure
- Largest cumulative emission (330 g N₂O ha⁻¹) measured on cattle manure cover
- N₂O emissions did not correlate with either WFPS or soil temperature
- Upscaling on ha-scale basis was done by multiplying the cumulative emission of N₂O linked the area of each crop type in the township
- The stratification by crop type was useful at identifying emission differences among the sites (wheat > canola > peas)
- For this relatively homogenous region, however, the area-weighted mean for cumulative emissions differed little from the non-area-weighted mean


Measuring and modeling N₂O fluxes at the field scale


- The model ecosys was run in 3D mode to simulate N₂O fluxes from a fertilized field with topographic variations
- Modeled data were compared with field scale measurements made using eddy covariance towers and a tunable diode laser trace gas analyzer
- Large spatial and temporal variability of N₂O emissions were modeled and measured
- Spatial and temporal aggregation of emissions to regional scales should not be based upon modeled or measured values of individual sites at time steps of a day or more
- Aggregation should rather be based upon diurnal values from typical landscapes within a region in which variation of surface topography and soil type is accurately represented

Observed (symbols) and modeled (lines) N₂O fluxes
Summary

- Nitrous oxide is an important greenhouse gas and agriculture plays a major role in its emission.
- Several options to reduce N₂O losses from agricultural soils:
  - Optimize N rates
  - Synchronize N applications with N demand by crop
- Monitoring:
  - Direct methods
  - Indirect methods
    - Accounting
    - Models
- An efficient system to monitor N₂O fluxes in agriculture should include a combination of direct (gas sampling) and indirect methods (accounting and models):
  - Aircraft monitoring will be possible in the future

Acknowledgements

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  - Integrated Assessment Research
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