Denitrification, nitrous oxide emissions and the EPA

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Greenhouse effect

- Sun's short waves
- Infrared rays radiate from ground and cannot pass through the glass
- Long wavelengths radiated to the atmosphere
- Short waves heat the ground
- Warmed air rises and heats the greenhouse
Nitrous oxide (N$_2$O) & climate change

$N_2O \rightarrow NO_x \rightarrow$ Ozone effect

$N_2O +$infrared $\rightarrow$ Climate Change

Source: Wuebbles 2009
Different greenhouse gases

The main greenhouse gases

<table>
<thead>
<tr>
<th>Greenhouse gases</th>
<th>Chemical formula</th>
<th>Pre-industrial concentration</th>
<th>Concentration in 1994</th>
<th>Atmospheric lifetime (years)***</th>
<th>Anthropogenic sources</th>
<th>Global warming potential (GWP)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon-dioxide</td>
<td>( \text{CO}_2 )</td>
<td>278 000 ppbv</td>
<td>358 000 ppbv</td>
<td>Variable</td>
<td>Fossil fuel combustion&lt;br&gt;Land use conversion&lt;br&gt;Cement production</td>
<td>1</td>
</tr>
<tr>
<td>Methane</td>
<td>( \text{CH}_4 )</td>
<td>700 ppbv</td>
<td>1721 ppbv</td>
<td>12.2 +/- 3</td>
<td>Fossil fuels&lt;br&gt;Rice paddies&lt;br&gt;Waste dumps&lt;br&gt;Livestock</td>
<td>21**</td>
</tr>
<tr>
<td>Nitrous oxide</td>
<td>( \text{N}_2\text{O} )</td>
<td>275 ppbv</td>
<td>311 ppbv</td>
<td>120</td>
<td>Fertilizer&lt;br&gt;industrial processes&lt;br&gt;combustion</td>
<td>310</td>
</tr>
<tr>
<td>CFC-12</td>
<td>( \text{CCl}_2\text{F}_2 )</td>
<td>0</td>
<td>0.503 ppbv</td>
<td>102</td>
<td>Liquid coolants&lt;br&gt;Foams</td>
<td>6200-7100 ****</td>
</tr>
<tr>
<td>HCFC-22</td>
<td>( \text{CHClF}_2 )</td>
<td>0</td>
<td>0.105 ppbv</td>
<td>12.1</td>
<td>Liquid coolants</td>
<td>1300-1400 ****</td>
</tr>
<tr>
<td>Perfluoromethane</td>
<td>( \text{CF}_4 )</td>
<td>0</td>
<td>0.070 ppbv</td>
<td>50 000</td>
<td>Production of aluminium</td>
<td>6 500</td>
</tr>
<tr>
<td>Sulphur hexa-fluoride</td>
<td>( \text{SF}_6 )</td>
<td>0</td>
<td>0.032 ppbv</td>
<td>3 200</td>
<td>Dielectric fluid</td>
<td>23 900</td>
</tr>
</tbody>
</table>

Note: ppbv: 1 part per billion by volume; ppmv: 1 part per million by volume

* GWP for 100 year time horizon. ** Includes indirect effects of tropospheric ozone production and stratospheric water vapour production. *** On page 15 of the IPCC SAR. No single lifetime for CO\(_2\) can be defined because of the different rates of uptake by different sink processes. **** Net global warming potential (i.e., including the indirect effect due to ozone depletion).

Source: IPCC radiative forcing report, Climate change 1995. The science of climate change, contribution of working group 1 to the second assessment report of the intergovernmental panel on climate change, UNEP and WMO, Cambridge press university, 1996.
U.S. GHG Emissions

Greenhouse Gas Emissions
United States, 2009
Carbon Dioxide 83%
Methane 10%
Nitrous Oxide 5%
HFCs, PFCs, SF₆ 2%

Source: US EPA 2007

U.S. greenhouse gas emissions by economic sector, 2008

6956.8 TG CO₂ Eq.
- Residential 5.2%
- U.S. territories 0.7%
- Commercial 5.9%
- Agriculture 7.2%
- Industry 19.3%
- Electric power industry 34.6%
- Transportation 27.1%

Agriculture and nitrous oxide

Relative Contribution of N$_2$O emission in United States

- Agri Soil Mgmt: 78%
- Production: 11%
- Others: 5%
- Combustion: 6%
$\text{N}_2\text{O}$ emission from cropped soil

Source: USDA
Agriculture and nitrous oxide

Source: USEPA 2009

Cut-away view of a representative section of a managed soil; histosol cultivation is represented here.
Microbial sources of soil $\text{N}_2\text{O}$

1. Denitrification

$$\text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$$

2. Nitrifier denitrification

$$\text{NH}_3 \rightarrow \text{NH}_2\text{OH} \rightarrow \text{NO}_2^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$$

3. Nitrification

$$\text{NO}_3^- \rightarrow \text{NO} \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2$$

4. Nitrate ammonification

$$\text{NH}_4^+ \rightarrow \text{NO}_2^- \rightarrow \text{N}_2\text{O}$$
Microbial sources of soil $\text{N}_2\text{O}$

1. Denitrification

$\text{NO}_2^-$ → NO → $\text{N}_2\text{O}$ → $\text{N}_2$

Nitrification

$\text{NO}_3^-$ → $\text{NH}_3$ → $\text{NH}_2\text{OH}$ → NO → $\text{N}_2\text{O}$ → $\text{N}_2$
Microbial sources of soil $N_2O$

1. Nitrate ammonification
   \[ \text{NH}_3 \rightarrow \text{NH}_2\text{OH} \rightarrow \text{NO}_2 \rightarrow \text{NO} \rightarrow N_2O \rightarrow N_2 \]

2. Nitrifier denitrification

3. Nitrification

$N_2O$
3. Nitrification

\[ \text{NH}_3 \rightarrow \text{NH}_2\text{OH} \rightarrow \text{NO}_2^- \]

\[ \text{N}_2\text{O} \]

\[ \text{NO}_3^- \]
4. Nitrate ammonification

\[ \text{NH}_4^+ \rightarrow \text{NO}_3^- \rightarrow \text{NO}_2^- \rightarrow \text{N}_2\text{O} \rightarrow \text{N}_2 \]

Microbial sources of soil $\text{N}_2\text{O}$
Measuring $\text{N}_2\text{O}$ emission

- **Bottom-up** - soil surface gas flux and models (DAYCENT) based on soil N application
- **Top-down** - changes in concentration of atmospheric $\text{N}_2\text{O}$ and sink estimates
- At sufficiently large scales, the use of both approaches yield similar estimates
- “convergence of ...approaches increases confidence...rudimentary understanding of factors controlling large spatial & temporal scales.” – Del Grosso et al. (2008)
Measuring soil $\text{N}_2\text{O}$ emission

- Chamber-based gas flux measurement

Source: http://www.ars.usda.gov/research/GRACEnet

$\text{N}_2\text{O}$ concentration in air sample is measured by Gas chromatograph with ECD detector
\[ \text{N}_2\text{O} \text{ emission reduction protocol (NERP)} \]

- \[ N_2O_{(\text{Reduction})} = N_2O_{+N(Before)} - N_2O_{+N(After)} \]

\[ N_2O_{+N(B/A)} = \left[ (F_{SN} + F_{ON}) \times EF_n \right] + N_2O_{0N(B/A)} \times \{N_2O_{MW}\} \times N_2O_{GW\text{P}} \]

\[ \downarrow \quad \downarrow \quad \downarrow \quad \downarrow \]

Organic N quantity \quad N_2O @ control \quad 44/28 \quad 298

Fertilizer N quantity

\[ EF = 0.012 \times \exp[0.00475 \times (F_{SN} + F_{ON})] \]

Source: Millar et al. 2010
Controls of denitrifier activity

- Soil nitrogen availability
- Organic matter
- Soil oxygen concentration
- Soil pH
- Soil temperature
Soil N availability & Fertilizer N

4 Factors control the soil N availability and N$_2$O emissions during growing season

1. Quantity (Full, split)
2. N source (NH$_4$/NO$_3$ based, inhibitor)
3. Application time (Early spring vs. late spring)
4. Application zone/place (side-dress/dribbled)
Fig. 4  Average daily N$_2$O flux during the 2008 growing season. Results from regression analysis [Eqns (1) and (2)] are shown for the best-fit model using the treatment averages from each site. Error bars represent standard error of the treatment averages.
Fertilizer N sources effect on N₂O

Glyndon, Wheat

Figure 3. 2009 Daily N₂O Soil Flux. Control= no treatment; ESN=environmentally smart nitrogen; NSN-nutrisphere N; SuperU=Urea with agrotain mixed in a pelletized form; Urea.

Figure 4. Cumulative soil N₂O-N losses in the 2009 growing season. Control= no treatment; ESN=environmentally smart nitrogen; NSN-nutrisphere N; SuperU=Urea with agrotain mixed in a pelletized form; Urea.

Source: Smith 2010
Fertilizer N sources effect on $N_2O$

Cumulative $N_2O$-N flux and percent fertilizer induced $N_2O$-N under a strip till corn, clay loam soils of CO

ESN_ssb = Polymercoated urea subsurface banded, Nfus = Nfusion and Agrot = AgrotainPlus

Source: Halvorson et al. 2011
Fertilizer N sources - N$_2$O loss - grain yield

**N$_2$O-N emission as a function of grain yield and grain N-uptake**

- **Urea**: 12.2a
- **ESN_ssb**: 7.3b
- **ESN**: 6.1bc
- **SuperU**: 5.6bcd
- **UAN**: 6.8bc
- **UAN+Nfus**: 5.3cd
- **UAN+Agrot**: 3.8d

ESN_ssb = Polymercoated urea subsurface banded, Nfus = Nfusion and Agrot = AgrotainPlus

Source: Halvorson et al. 2011
Timing influences $N_2O$ emission

Cumulative Nitrous Oxide Fluxes for Field Plots Fertilized Early vs. Late Spring

Silt loam, Mandan, ND, Corn, April 1 vs. May 15

Source: Philips et al. 2009
Placement influences $\text{N}_2\text{O}$ emission

Deep placement increase the $\text{N}_2\text{O}$ emission by 26% for in clay loam soils in eastern Canada!

Source: Drury et al. 2006
Placement influences $\text{N}_2\text{O}$ emission

50% reduction in $\text{N}_2\text{O}$ emission from change of 5 to 10 cm for both tillage practice for fine loamy corn soil, CO

Tillage and placement treatment significant at 90% sign. level

Liu et al. 2006
# Fertilizer induced N₂O emission reduction

<table>
<thead>
<tr>
<th>Performance Level</th>
<th>Right Source</th>
<th>Right Rate</th>
<th>Right Time</th>
<th>Right Place</th>
</tr>
</thead>
<tbody>
<tr>
<td>Basic</td>
<td>*NH₄ based</td>
<td>*Recommended</td>
<td>*Apply in spring *Split *Fall (&lt;50°F)</td>
<td>Bands/Injection</td>
</tr>
<tr>
<td>Intermediate</td>
<td>*NH₄ based</td>
<td>*Soil test *landscape *soil variability</td>
<td>*Apply in spring *Split *Fall (&lt;50°F) + inhibitor</td>
<td>Bands/Injection</td>
</tr>
<tr>
<td>Advanced</td>
<td>*NH₄ based</td>
<td>*Digitized soil maps *grid sampling *satellite imagery *real time crop sensors *Seasonal crop monitoring</td>
<td>*Apply in spring *Split *Fall (&lt;50°F) + inhibitor</td>
<td>Bands/Injection</td>
</tr>
</tbody>
</table>
Tillage and Soil texture control

Crop - Barley and location: Quebec City, Canada

Source: Rochette et al. 2008
Precision tillage reduced N$_2$O emission

Precision till – Nu-Till (Ag Spectrum) utilizing
(1) Martin row cleaners,
(2) Keeton seed firmers,
(3) Martin spader and
(4) a dagger chain
Soil- Silt loam
Lafayette, In

Source: Smith et al. 2011
Above normal precipitation triggers tile use

North Dakota: July, 2011 Monthly Departure from Normal Precipitation
Valid at 8/1/2011 1200 UTC - Created 8/3/11 21:40 UTC
Tile facilitates stand establishment

- Warm up and dry out the soils in spring
- Allows earlier field operations
- Optimum soil moisture condition
- Root development
Soil porosity controls N$_2$O formation
Tile and N$_2$O emissions

- **Fertilizer N rate (±?)**
- **Plant N uptake (+)**
- **N mineralization rate/availability (+)**
- **Denitrification loss of N$_2$O (+?)**
- **Drainage loss (-) of NO$_3^-$**
Soil management practices to reduce N₂O
EPA’s stands on GHG emission

• The Clean Air Act of 1970 requires EPA to curb the emissions of any air pollutant

• Since its enactment, GDP rise to 207%, 1.6 million jobs and $40 billion in exports

• Supreme court ruled out 2007 case Massachusetts vs. EPA that GHG are chemical substance emitted into the air and are air pollutants
EPA Taking action under the law

- EPA issued “endangerment finding in 2009: GHG, a threat to public health, welfare and climate.
- First phase, safeguard’s for power plants and oil refineries enacted on January 2, 2011
- Clean Car Agreement: 35.5 mpg by 2016
- New EPA standards were “a victory for car companies...pay less at the pump; for our security, and for the environment as we reduce pollution” – President Barack Obama
EPA’s Tailoring Rule

- July 1, 2011: emit $>100,000$ tons yr$^{-1}$ required operating permits to account for GHG
- By June 30, 2013: 550 sources need to obtain operating permits
- 900 new facilities per year will trigger New Source Review permitting requirements
- emit $>50,000$ tons yr$^{-1}$ will not be subject to permitting requirements until at least April, 2016
- Every State (except Texas) says they are ready to enact EPA safeguards
Thanks for your patience

Questions and comments

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