Nitrous Oxide Monitoring in Agriculture

R. César Izaurralde
Joint Global Change Research Institute
www.globalchange.umd.edu

Agriculture's Role in the New Carbon Economy
CASMGS Forum

Manhattan, KS
17-18 December, 2007

UNIVERSITY OF MARYLAND

JGCRI
Joint Global Change Research Institute

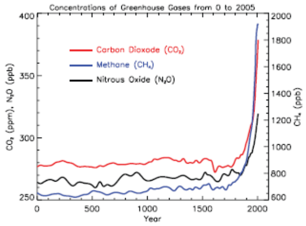
Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy

Outline

- Introduction
  - Nitrous oxide and global warming
  - Nitrous oxide and agriculture
- How do soils generate N_2O?
- What factors affect N_2O production in soils?
- How can we monitor N_2O fluxes?
  - Direct methods
    - Chambers (manual, automatic)
    - Tunable diode laser absorption spectroscopy
    - Isotopic (^{15}N)
  - 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

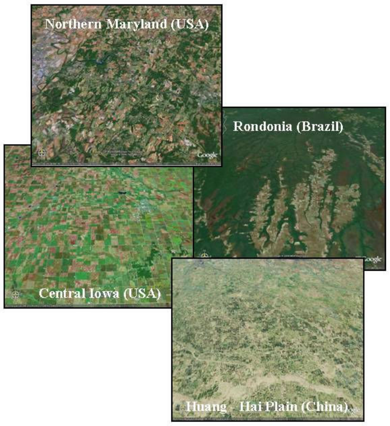
- Human activities result in emissions of four principal greenhouse gases: CO_2, CH_4, N_2O and the halocarbons (a group of gases Fl, Cl and Br)
- Atmospheric concentrations of long-lived greenhouse gases have been increasing over the last 2,000 years, especially since 1750 –the beginning of the industrial 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 N_2O



	Concentrations and Δs (ppm)		Radiative Forcing	
	2005	Δ since 1998	2005 W m^{-2}	Δ since 1998 (%)
CO_2	379	13	1.66	13
CH_4	1.774	0.011	0.48	-
N_2O	0.319	0.005	0.16	11

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

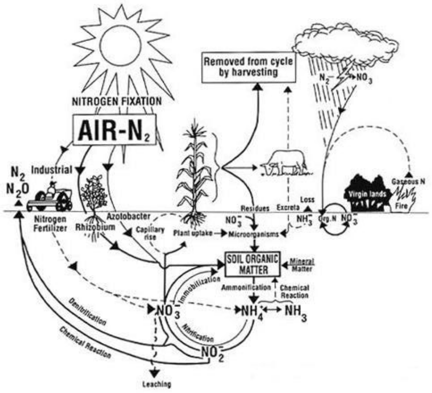
- Agricultural lands (cropland, grasslands and permanent crops) occupy about 40-50% of the Earth's land surface (13.4 Bha)
- Agricultural activities resulted in emissions of 5.1-6.1 $GtCO_2$-eq yr^{-1} in 2005 (10-12 % of total global anthropogenic emissions of greenhouse gases)
  - CH_4 contributes 3.3 $GtCO_2$-eq yr^{-1} (50% of total)
  - N_2O contributes 2.8 $GtCO_2$-eq yr^{-1} (60% of total)
  - CO_2 contributes 0.04 $GtCO_2$-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

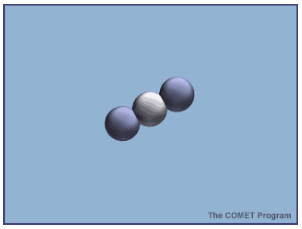
- The atmosphere is a major repository of nitrogen (N_2)
- Nitrogen accumulated in soils over geologic times due to a small imbalance between biological N fixation (gain) and denitrification (loss)
- Humans have altered the N cycle by
  - Industrial fixation of nitrogenous fertilizers
  - Manipulation of domestic animals, crop residues, and harvested products



http://ohioline.osu.edu/aex-fact/0463.html

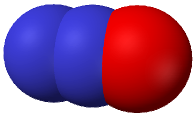
But, what is a “greenhouse gas” anyway?

- Nitrogen, O_2, and Ar make up for 99% of the atmosphere but are not greenhouse gases
- Water vapor, CO_2, CH_4, and N_2O 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

The N_2O molecule



$$N{\equiv}\overset{+}{N}{-}O^{-} \qquad {}^{-}N{=}\overset{+}{N}{=}O$$

And why is N_2O such as potent greenhouse gas? Two definitions and a formula

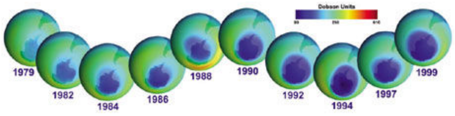
- Radiative Forcing: Change in net irradiance (W m^{-2}) at the tropopause after allowing stratospheric temperatures to re-adjust to radiative equilibrium, but with surface and tropospheric temperatures held at their unperturbed values
  - A positive value warms the system while a negative value cools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

$$GWP_{N2O} = \frac{N_2O(Wm^{-2}g^{-1}(100y)^{-1}}{CO_2(Wm^{-2}g^{-1}(100y)^{-1}}$$

- Nitrous oxide has a long lifetime in the atmosphere: 114 years
- The GWP for N_2O varies according to the time considered:
  - For 20 years: 310 gCO_2 $(gN_2O)^{-1}$
  - For 100 years: 298 gCO_2 $(gN_2O)^{-1}$

But before we continue with N_2O monitoring, let’s remind ourselves that N_2O also plays a role in the destruction of the stratospheric O_3 layer

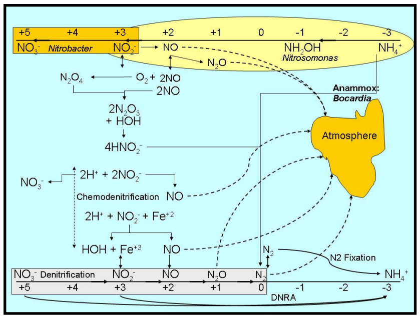
- The stratospheric O_3 layer protects life from harmful solar UV radiation
- Chlorofluorcarbons (CFCs) generate atomic chlorine, which catalyze the destruction of O_3
  - Montreal Protocol (1987)
- Nitrous oxide that reaches the stratosphere undergoes photolythic reactions, which lead to destruction of O_3
  - $N_2O + O(1D) \rightarrow 2NO$
  - $N_2O + O(1D) \rightarrow N_2 + O_2$



science.hq.nasa.gov/missions/satellite_22.htm

How does N_2O generate in soils?

- Nitrous oxide is generated in soils mainly by two processes:
  - Denitrification
    - Carried out by heterotrophic microbes under anaerobic conditions
    - $NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$
    - Denitrification is the sum of N_2O and N_2 loss
    - The ratio $N_2O/(N_2O+N_2)$ varies upon environmental conditions
  - Nitrification
    - Carried out by autotrophic microbes under aerobic conditions
    - $NH_4^+ \rightarrow NH_2OH \rightarrow \overset{N_2O \atop \uparrow}{NO} \rightarrow NO_2^- \rightarrow NO_3^-$
- Other pathways are possible
  - Chemodenitrification
  - Anammox
  - DNRA (Dissimilatory Nitrate Reduction to Ammonium)



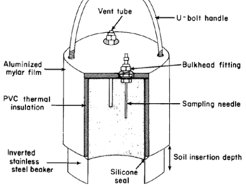
McGill et al. 2004. Agron. Abs. CD ROM

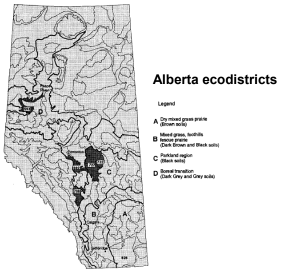
Monitoring N_2O fluxes at regional scales

Lemke et al. (1998) Soil Sci. Soc. Am. J. 62:1096–1102

- Objective: monitor N_2O fluxes at 6 locations in Alberta, Canada during 2 years (Summer 1993 – Spring 1995)
- Estimated losses of N_2O varied from year to year and from site to site
  - 0.4 kg N_2O-N ha^{-1} at Breton
  - 2.6 kg N_2O-N ha^{-1} at Eckville
- Losses of N_2O-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_2O-N

Hutchinson and Mosier (1981) Soil Sci. Soc. Am. J. 45:311–316





Lemke et al. (1998) Soil Sci. Soc. Am. J. 62:1096–1102

Automated chambers can provide much better temporal coverage than manually-operated systems

Automated chamber system used in Australia

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

Edwards et al. (2003) Agric. For. Meteor. 115:71-89

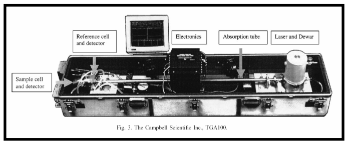
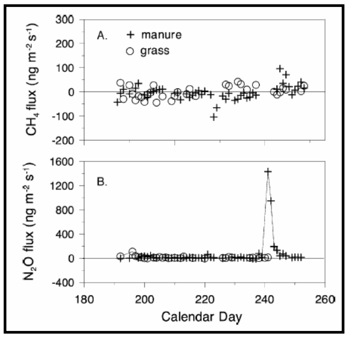


Fig. 3. The Campbell Scientific Inc., TGA100.

The Campbell Scientific Inc., TGA100

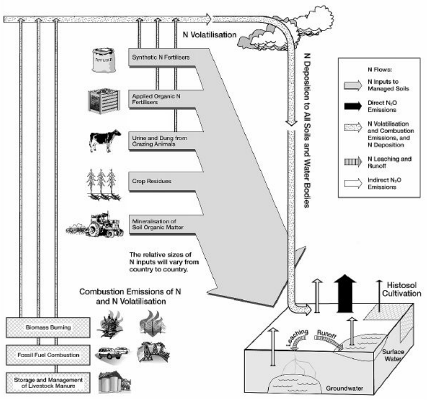
- Trace gases can be measured at field scale combining diode laser absorption spectroscopy and micrometeorological techniques
- Instrumentation offers rapid sampling rates to be used with eddy correlation and flux gradient techniques



CH_4 (A) and N_2O (B) fluxes from grass and fallow soil at Elora (Ontario) in 1992

2006 IPCC Guidelines for National Greenhouse Gas Inventories; Vol. 4, Ch. 11
(http://www.ipcc-nggip.iges.or.jp/public/2006gl/index.htm)

- Mostly for country or regional scale
- Three methodologies:
  - Tier 1: basic, direct N_2O emissions from managed soils estimated as:
    - $N_2O_{Dir}–N = N_2O–N_{Ninp} + N_2O–N_{OS} + N_2O–N_{PRP}$
    - 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)

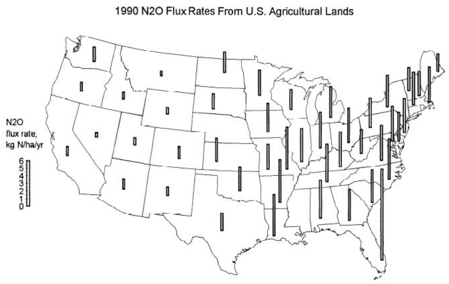


Sources and pathways of N that result in direct and indirect N_2O emissions from soils and waters

---

DNDC, a biogeochemical model to simulate soil cabon 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

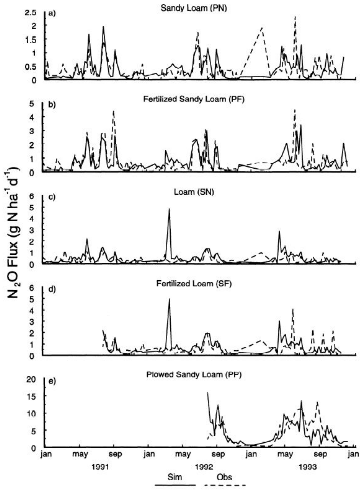


Li et al. (1996) Global Biogeochem. Cycles 10:297-306

Modeling N_2O and N_2 production generated from denitrification and nitrification processes

Parton et al. (1996) Global Biogeochem. Cycles 10:401-412

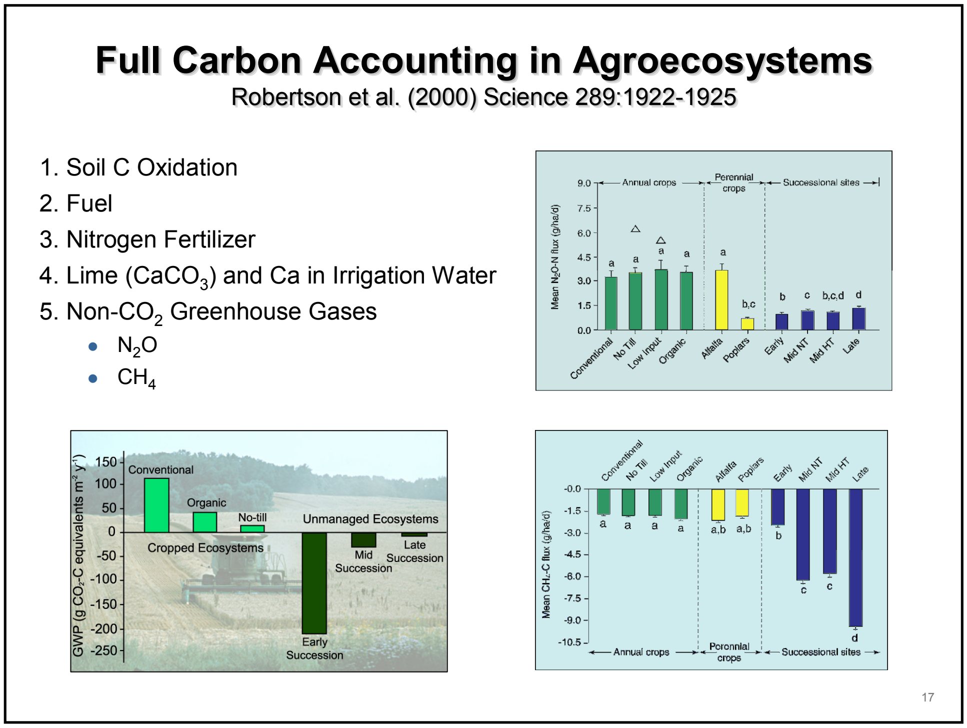
- Daily time step process-based model developed on the basis of the Century model
- Models nitrification as a function of soil pH, soil water content, soil temperature, and soil NH_4^+ level
- N_2O formation during nitrification is a direct function of nitrification rate
- N_2O and N_2 formation during 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

Robertson et al. Science 289:1922-1925 (2000)

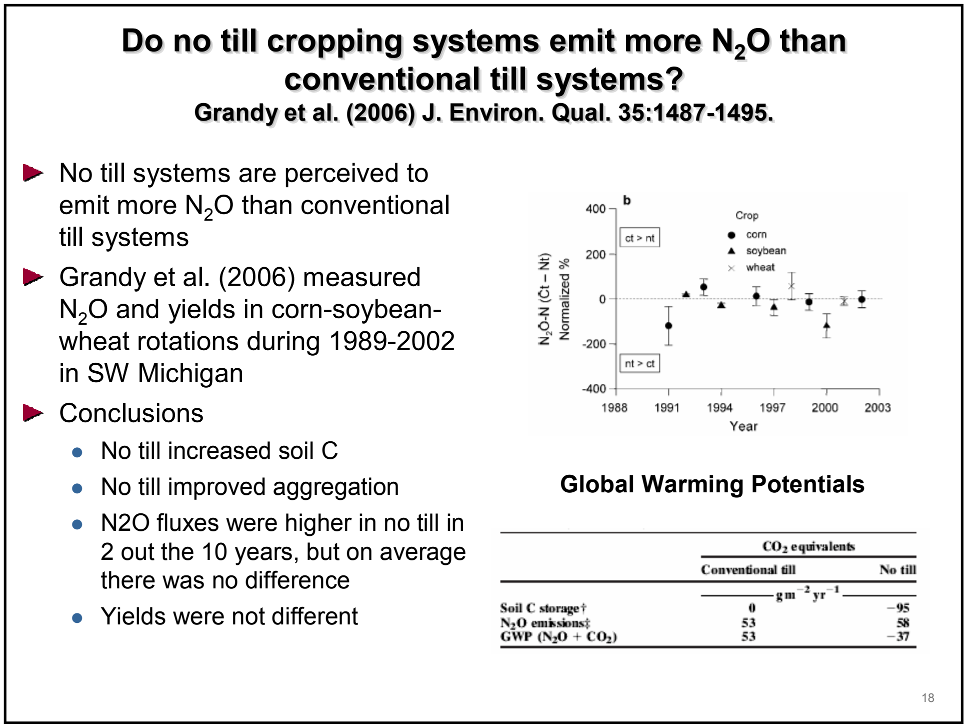
Ecosystem Type	**Management Intensity**
Annual Crops (Corn - Soybean - Wheat)	
Conventional tillage	High
No-till	
Low-input with legume cover	
Organic with legume cover	
Perennial Crops	
Alfalfa	
Poplar trees	
Successional Communities	
Early successional old field	
Mid successional old field	
Late successional forest	Low



Full Carbon Accounting in Agroecosystems

Robertson et al. (2000) Science 289:1922-1925

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_2O
   - CH_4



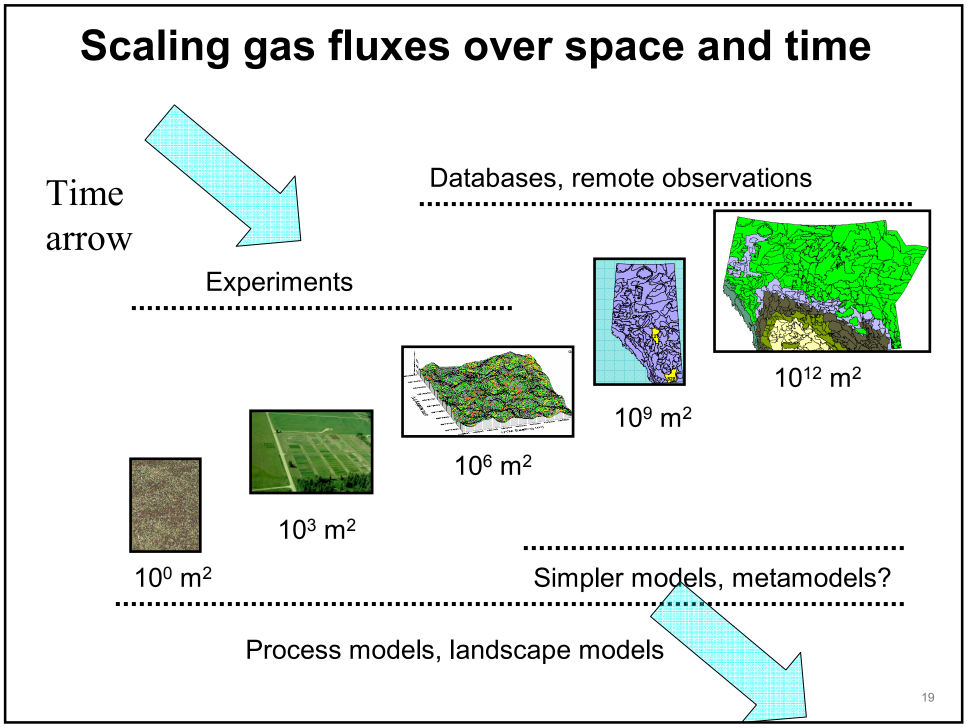
Do no till cropping systems emit more N_2O than conventional till systems?

Grandy et al. (2006) J. Environ. Qual. 35:1487-1495.

- No till systems are perceived to emit more N_2O than conventional till systems
- Grandy et al. (2006) measured N_2O and yields in corn-soybean-wheat rotations during 1989-2002 in SW Michigan
- 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

Global Warming Potentials

	CO_2 equivalents	
	Conventional till	No till
	$g\,m^{-2}\,yr^{-1}$	
Soil C storage†	0	−95
N_2O emissions‡	53	58
GWP (N_2O + CO_2)	53	−37



Scaling gas fluxes over space and time

Time arrow

Databases, remote observations

Experiments

10^{0} m^{2}

10^{3} m^{2}

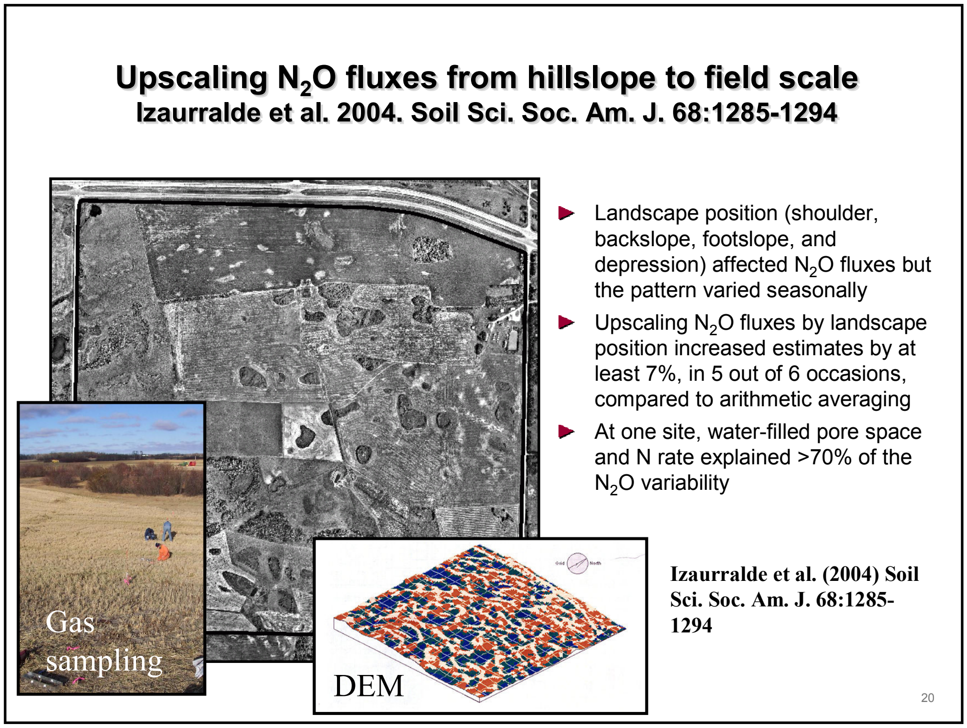
10^{6} m^{2}

10^{9} m^{2}

10^{12} m^{2}

Simpler models, metamodels?

Process models, landscape models



Upscaling N_2O fluxes from hillslope to field scale

Izaurralde et al. 2004. Soil Sci. Soc. Am. J. 68:1285-1294

- 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

Gas sampling

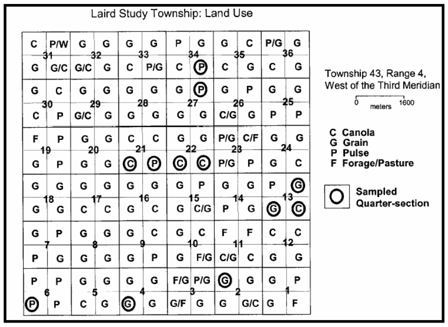
DEM

Izaurralde et al. (2004) Soil Sci. Soc. Am. J. 68:1285-1294

Upscaling N_2O fluxes from fields (40 ha) to township scale (9200 ha)

- N_2O 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 N_2O ha^{-1}) measured on cattle manure cover
- N_2O emissions did not correlate with either WFPS or soil temperature
- Upscaling on ha-scale basis was done by multiplying the cumulative emission of N_2O times 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

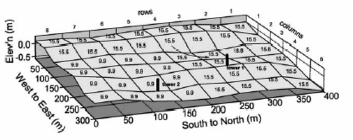
Pennock et al. (2005) Can. J. Soil Sci. 85:113-125



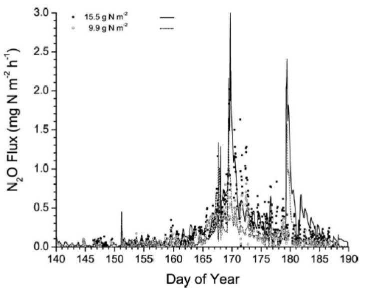
Measuring and modeling N_2O fluxes at the field scale

Grant and Pattey. (2003) Soil Biol. Biochem. 35:225-243

- The model *ecosys* was run in 3D mode to simulate N_2O 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 N_2O 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



N application and TDL towers



Observed (symbols) and modeled (lines) N_2O fluxes

Summary

- Nitrous oxide is an important greenhouse gas and agriculture plays a major role in its emission
- Several options to reduce N_2O 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 N_2O 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

- CASMGS
- US Department of Energy, Office of Science
  - Integrated Assessment Research
  - Carbon Sequestration in Terrestrial Ecosystems (CSiTE)
  - The Modeling of Regional Climate over China
- Robertson Foundation