Public Meeting for Contract 23RD017

Scientific Evaluation of Nitrogenous Emissions from Soils

Subject Matter Expert Review Panel (SMERP) on Nitrogenous Emissions
Feb 13, 2025

SMERP Members

- Dr. William Horwath, UC Davis
- Dr. Whendee Silver, UC Berkeley
- Dr. Xia Zhu-Barker, University of Wisconsin-Madison
- Dr. Martin Burger, Expert in Soil Nitrogen Emissions
- Dr. Viney Aneja, North Carolina State University

Scope of Work

Evaluate the current state of the science on nitrogenous (i.e., reactive nitrogen compounds) emissions from soils in California by providing quantitative evidence and comprehensive justifications that support the responses and conclusions set out by the committee, which will also answer specific questions posed in the Tasks of this contract.

This work will emphasize on emissions of air pollutants like oxides of nitrogen (NO_X), ammonia (NH_3), and nitrous oxide (N_2O) in agricultural regions where nitrogen fertilizers and organics are applied.

Task 1: Coordinate with the SMERP Members and Moderate Bi-Monthly Meetings

- SMERP members will coordinate to address specific questions on nitrogenous emissions from California’s soils, as posed in Task 2.

- SMERP members will objectively and critically provide detailed and comprehensive answers that leverage their knowledge and other existing scientific materials.

- SMERP members will synthesize all the responses and seek consensus during bi-monthly meetings.

- SMERP members will synthesize all the information that derived from this contract into a comprehensive report.

Task 2: Conduct a comprehensive review of nitrogenous emissions from soils

APPROACH: Review of scientific literature, pertinent databases, and emission estimation methodologies

- What scientific data sources are there on nitrogenous emissions from soils (e.g., NO_X, NH_3, N_2O)? Review of past and current literature.
- Classify scientific data sources in a database that clearly describes the spatial (e.g., San Joaquin Valley, Imperial Valley) and the temporal (e.g., seasonal, annual, daily) relevance to California, including agronomic production practices.
- Describe driving variables (e.g., activity data, application method, nitrogen content, soil moisture, temperature, etc.) for nitrogenous emissions from soils.

Task 2: Conduct a comprehensive review of nitrogenous emissions from soils (cont.)

- Assess the importance of nitrogenous emissions in comparison to literature studies.
- Assess the uncertainty of modeling of nitrogenous emissions.
- Inform CARB of study synthesis on ways to refine CARB’s emission inventory.
- Identify any knowledge gaps that could be addressed through additional research and field studies to ensure that future research efforts are effective and informative.

Deliverables

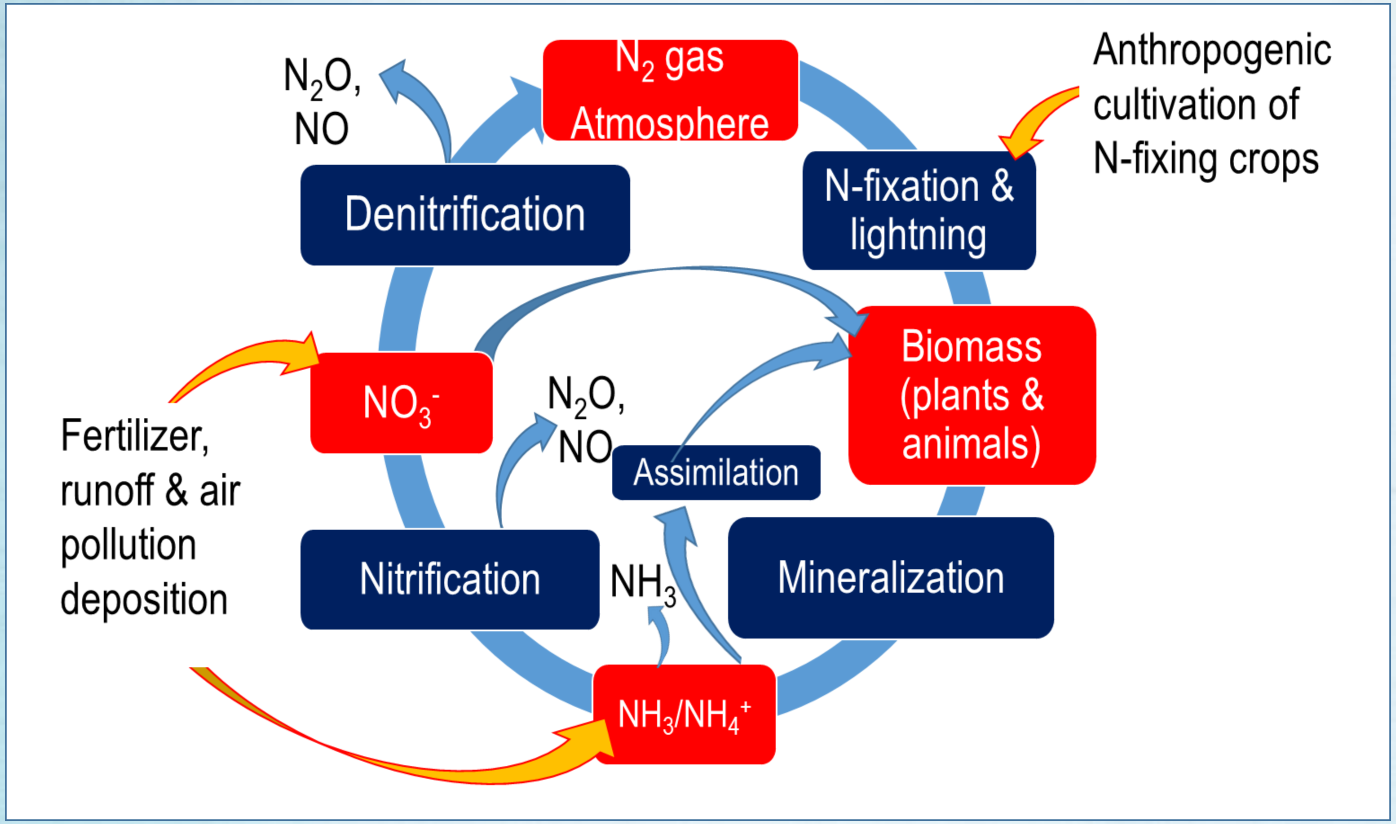
- Draft Final Report (April 1) and virtual or in-person seminar (June)
- The Final Report will include content from the Draft Final Report that has been refined based on the comments provided throughout the process.
- Peer-reviewed publications, if any, will be publicly available.

Project Progress

- Collected published articles, white papers, technical report, and EPA and CARB databases.
- Summarized factors and controls of nitrogenous emissions from soils.
- Reviewed emission methodologies and modeling estimations
- Compared reported uncertainties of different methodologies

Background

Introduction: The Soil Nitrogen Cycle



The nitrogen cycle in soils/water/biosphere and its connection with the atmosphere.

Source: Battye, Aneja, and Schlesinger, 2017.

- The nitrogen cycle is the biogeochemical cycle by which nitrogen is converted into multiple chemical forms as it circulates **among atmosphere, biosphere, hydrosphere and lithosphere** ecosystems.
- Important processes in the nitrogen cycle include **fixation, mineralization, assimilation, nitrification, and denitrification**.

NOx Sources and Reactions of Ozone Formation

NO (nitric oxide) + NO_2 (nitrogen dioxide) = NOx
Acts as catalyst in the formation of O_3 (ozone).

$$NO + HO_2 \rightarrow NO_2 + OH^-$$

$$NO + O_3 \rightarrow NO_2 + O_2$$

$$NO_2 + hv \rightarrow O + NO$$

$$O + O_2 + M \rightarrow O_3 + M$$

Further reactions of NO_2 in the atmosphere, e.g. HNO_3 (g)
Precursor of ambient particulate (PM 2.5) nitrate

Sources of NOx: Nitrification by soil microbes (denitrification minor source)
HONO, the gaseous form of nitrous acid (HNO_2) produced by soil microbes

Other Sources: Fuel combustion
Biomass burning
Lightning

Driving Factors & Environmental Controls for Soil NOx Emissions

NH_4 availability:	Substrate for nitrification close to the soil surface
Soil Temperature:	Exponential rise in NO emissions between 15 -35°C
	Between 15 -35°C approximate doubling of NO emission rate for each 10°C rise.
	Exponential rise of NO emissions and other functions up to 40°C have been proposed.
Soil Moisture:	Must be sufficient for nitrification, but high soil water content limits gas transport and increases potential consumption of NO (e.g. nitrous oxide production).
	Denitrification (minor source)
Soil pH:	Low pH inhibits complete nitrification
	Low pH drives abiotic production of NO and HONO

Methods & Instrumentation

Soil NOx emissions:

- Manual soil cover method with dynamic or static chamber to measure soil-to-atmosphere NO flux: Direct measurement, represents a small footprint, laborious, fewer measurements/potentially large variance.
- Flux tower data becoming more available for NOx emissions.
- HONO measurement requires Long Path Absorption photometer (LOPAP).

Tropospheric NO_2 concentrations:

- Surface monitors with NOx analyzers and spectrometer instruments to measure ambient NO_2.
- Aircraft equipped with NOx analyzers to measure in-situ NO_2.
- Pandora: Ground-based sun-viewing spectrometers to derive tropospheric NO_2 vertical column densities from total (stratospheric & tropospheric) column densities.
- Remote sensing instruments mounted on satellites (OMI, TROPOMI) to retrieve total, stratospheric, and tropospheric NO_2 column densities.

Methods & Instruments: Nitrous oxide (N_2O)

Soil N_2O emissions:

- Characterized by hot spots and hot moments and thus can vary by orders of magnitude over short time scales and small spatial extent
- Requires high replication in space and time
- Irrigation (soil moisture) and fertilization are important drivers
- Cavity ringdown spectroscopy allows for continuous flux measurements
- Eddy covariance can capture soil-atmosphere exchange at an ecosystem scale
- Expensive and technologically challenging

Methods & Instruments: Ammonia (NH_3)

Soil NH_3 emissions:

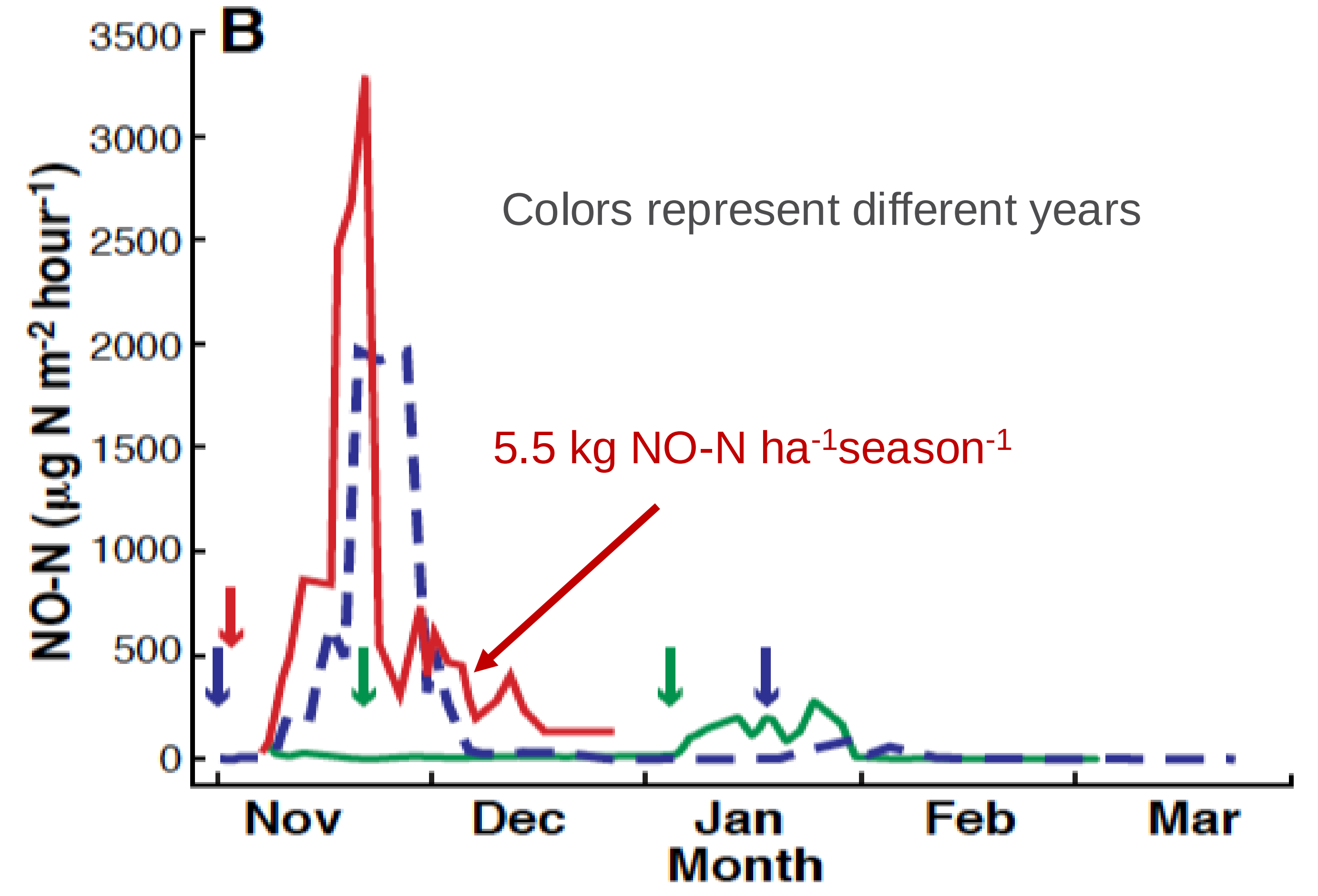
- "Sticky" gas that is readily soluble
- Requires non-stick surfaces for chambers and tubing, and temperature controlled lines to minimize solubilization
- Instruments must also be lined with non-stick materials
- Cavity ringdown spectroscopy allows for continuous flux measurements
- Likely characterized by hot spots and hot moments
- Expensive and technologically challenging

Atmospheric NH_3 emissions:

- Generally point measurements
- Annular denuder with acid trap
- Passive samplers
- Quantum laser and chemiluminescence analyzer

Direct Measurements of Soil NOx Emissions

- Lack of long-term direct NO flux measurements in arid irrigated systems



Colors represent different years

5.5 kg NO-N ha^{-1} $season^{-1}$

- Comparable seasonal data sets are lacking from California

Matson et al. 1998. Irrigated wheat fertilized with 250 kg N ha^{-1} at CIMMYT, Sonora, Mexico.

Direct Measurements of annual Soil NOx Emissions in California are lacking: we have only averages

Average growing season NOx fluxes from California cropping systems:

Reference	g NO-N ha^{-1} hr^{-1}	# of sites	# of measurements
Matson & Firestone 1995	0.1 -0.9	26	2850
Burger & Horwath 2013	0.04 – 1.35	14	1155
Oikawa et al. 2015	2.3 – 4.6	2	66

Max. NOx fluxes observed (“hot moments”) growing season

	g NO-N ha^{-1} hr^{-1}
Williams et al. 1992	12 (no error reported)
Matson et al. 1998	45 (+/- 14)
Burger & Horwath 2013	42 (+/- 13)
Oikawa et al. 2015	32 (no error reported)

- **Problem not <u>capturing annual flux</u> therefore possibly underestimating emissions**

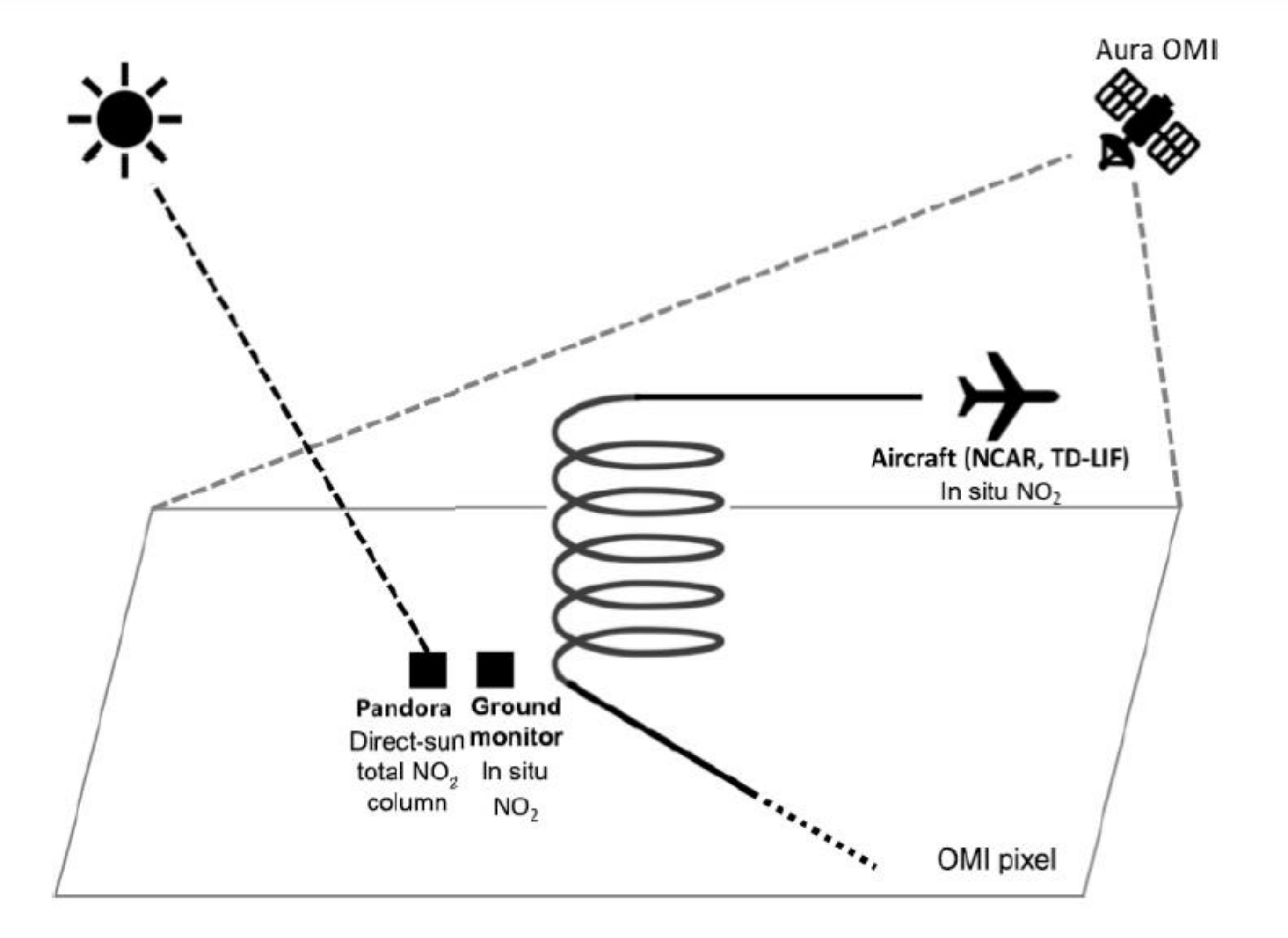
Modeling Soil NOx Emissions

- Air quality models (e.g. Biogenic Emissions System, Community Multiscale Air Quality) require mechanistic representation of biogeochemical processes, land management practices, and meteorological conditions as inputs.
- Temperature, soil moisture, and timing, quantity, and types of fertilizer inputs have profound impacts on NOx emissions from cropland.
- Models can be linked to databases and sub-models (e.g. EPIC, DayCent) to specify these inputs.
- However, calibration (often missing) and validation of modelling results is difficult due to lack of comprehensive seasonal data.

Validating Modelled Soil NOx by remote Sensing

- Tropospheric NO_2 column amounts derived from satellite-mounted instruments include NO_2 from all sources.
- Each source (natural vs anthropogenic) has its own uncertainty.
- Retrieval of NO_2 column densities requires the use of accurate assumptions, such as atmospheric chemistry, meteorology, and air-mass factors.
- Satellite-derived values have a large footprint.
- NO_2 confined to local scale with respect to source
- Uncertainty of soil NOx emissions in ecosystems other than cropland (shrubland, forests, urban lawns).

NO_2 Observations at Different Scales



Footprints and uncertainties vary among instruments and methods:

- Satellite mounted OMI: 312 km^2
- Aircraft spirals ascents: 4 km dia., descents 10-20 km dia.
- Ground monitors & Pandora are point measurements.

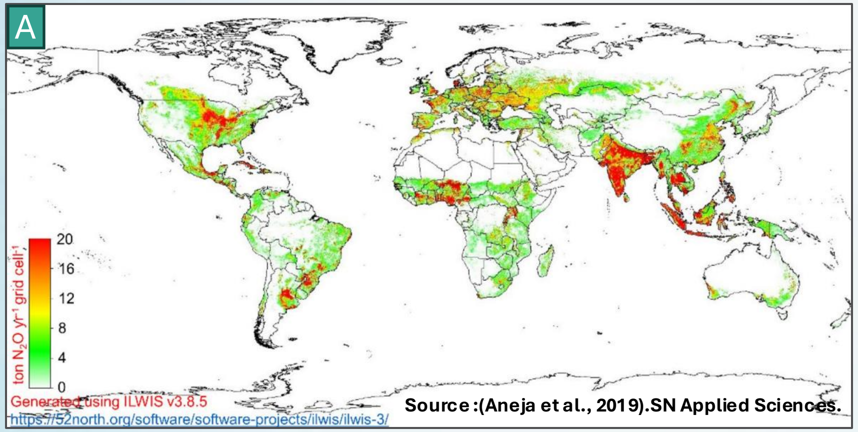
From: Choi et al. (2020) NASA DISCOVER-AQ campaign 2011-2013

Uncertainties of Estimates

Reference	Model	% Soil NOx / total NOx*	Area
Yienger & Levy 1995	Y&L	15 - 20	CONUS
Jaegle et al. 2005	GEOS-CHEM	22	CONUS
Rasool et al. 2019	CMAQ	10 - 13	CONUS
Hudman et al. 2012	BDSNP	20 - 33	CONUS
Sha et al. 2021	BDISNP	40	California
Guo et al. 2020	DNDC	1.1	California
Aneja et al. 2021	NO-STAT	1.2 -2.8	Worldwide

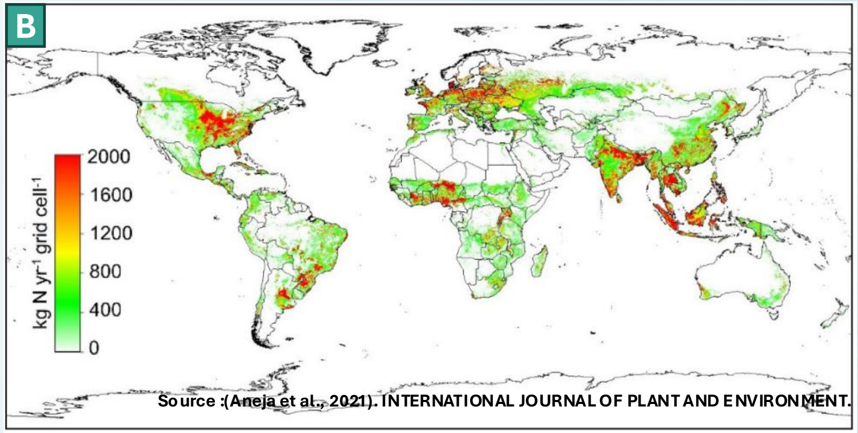
* Huge uncertainty in total NOx

Characterization of Atmospheric Reactive Nitrogen Emissions from Global Agricultural Soils



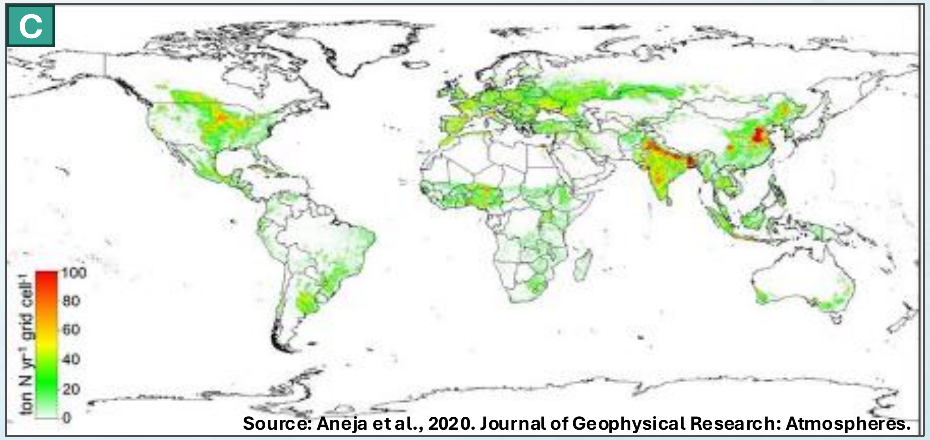
Source :(Aneja et al., 2019).SN Applied Sciences.

Global Atmospheric N_2O emissions from agricultural sources



Source :(Aneja et al., 2021). INTERNATIONAL JOURNAL OF PLANT AND ENVIRONMENT.

Global Atmospheric NOx emissions from agricultural sources

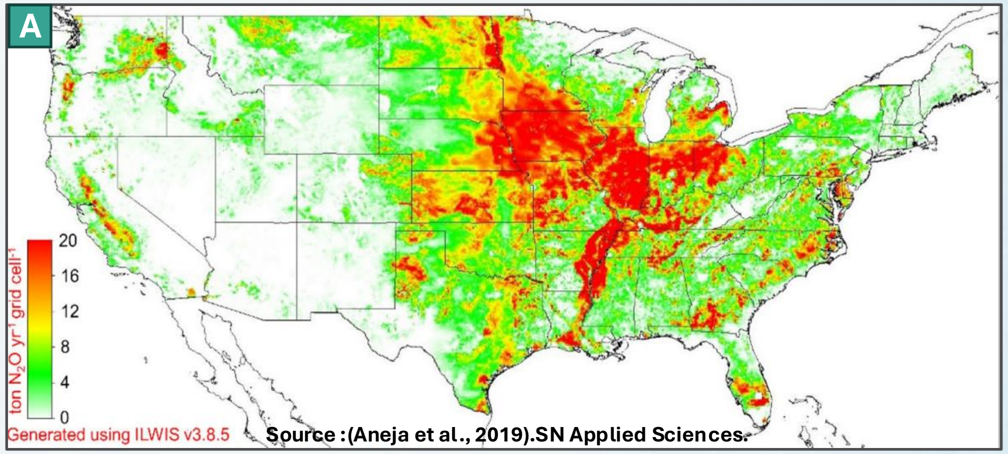


Source: Aneja et al., 2020. Journal of Geophysical Research: Atmospheres.

Global Atmospheric NH_3 emissions

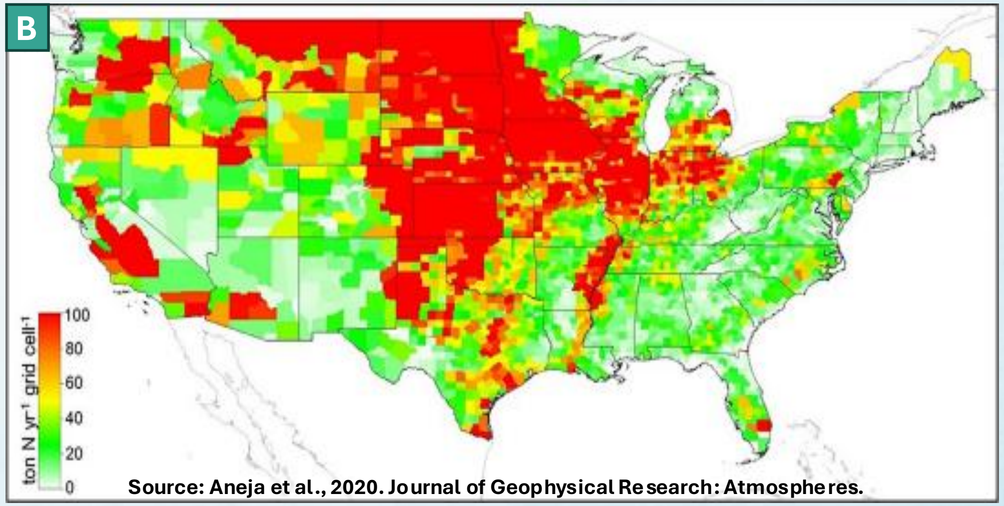
Atmospheric Reactive Nitrogen Emissions from Global Agricultural Soils

From US Agricultural Soils



Source :(Aneja et al., 2019).SN Applied Sciences.

CONUS Atmospheric N_2O emissions from agricultural sources



Source: Aneja et al., 2020. Journal of Geophysical Research: Atmospheres.

CONUS Atmospheric NH_3 emissions from agricultural sources

- **Paucity of NOx emissions measurements in the US**

Atmospheric Reactive Nitrogen Emissions from Continental United States Agricultural Soils

Conclusions

- Lacking seasonal data to inform prediction efforts
- Modeling Soil NOx Emissions limited validation
- Uncertainties of soil NOx Emission Estimates
- Analyze the spatial distribution of California and global reactive N (Nr) emissions from agricultural soil to improve prediction
- Data paucity is limiting our ability to make critical decisions on sources (soil vs other) and informed mitigation outcomes