## Public Meeting for Contract 23RD017

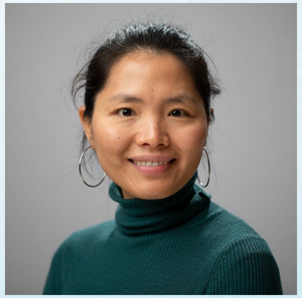
# Scientific Evaluation of Nitrogenous Emissions from Soils

Subject Matter Expert Review Panel (SMERP) on Nitrogenous Emissions

July 11, 2025

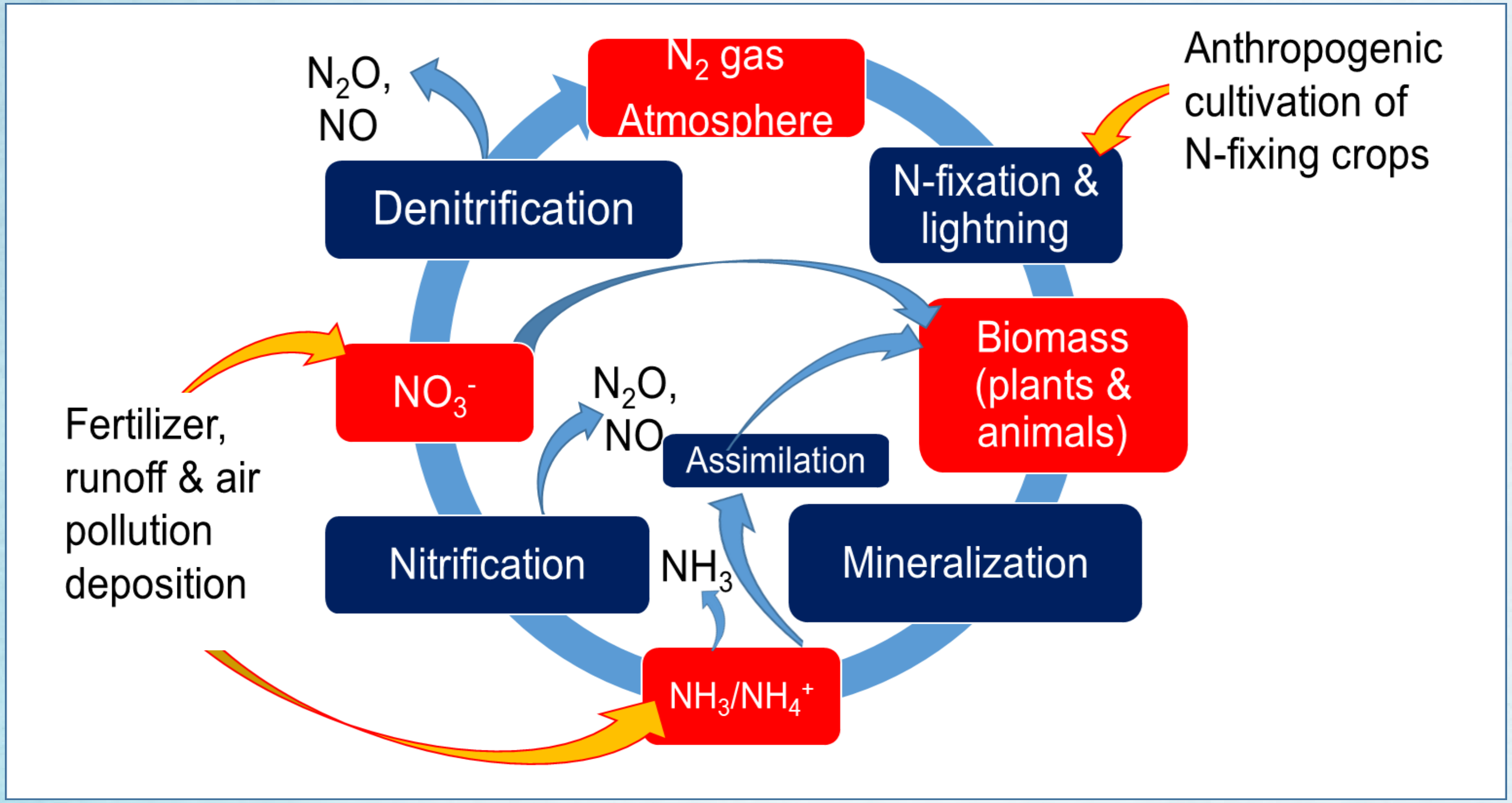
# SMERP Members

- 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

# Background

## ***Introduction: The Soil Nitrogen Cycle***



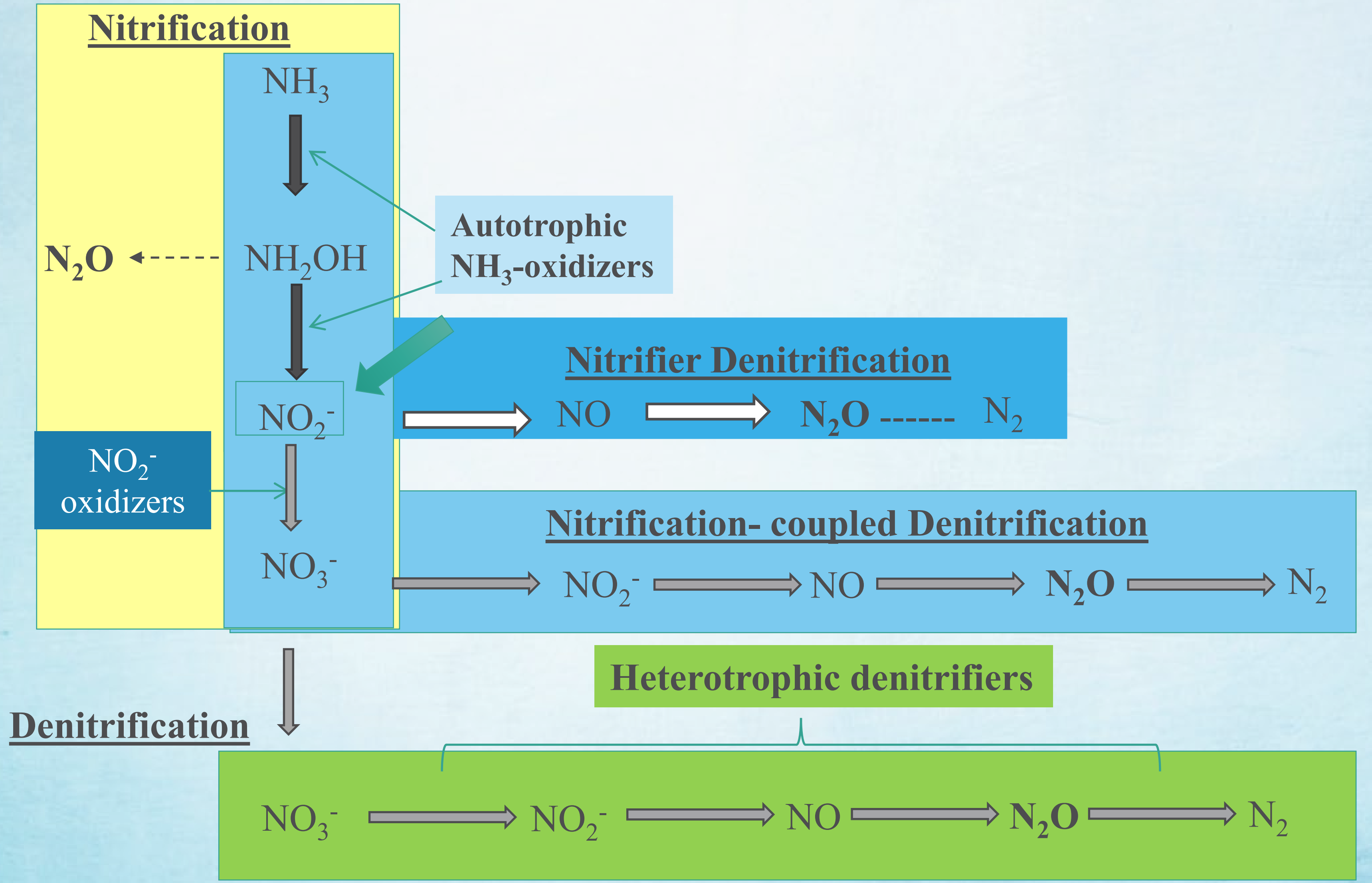

**The nitrogen cycle in soils/water/biosphere and its connection with the atmosphere.**

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**.

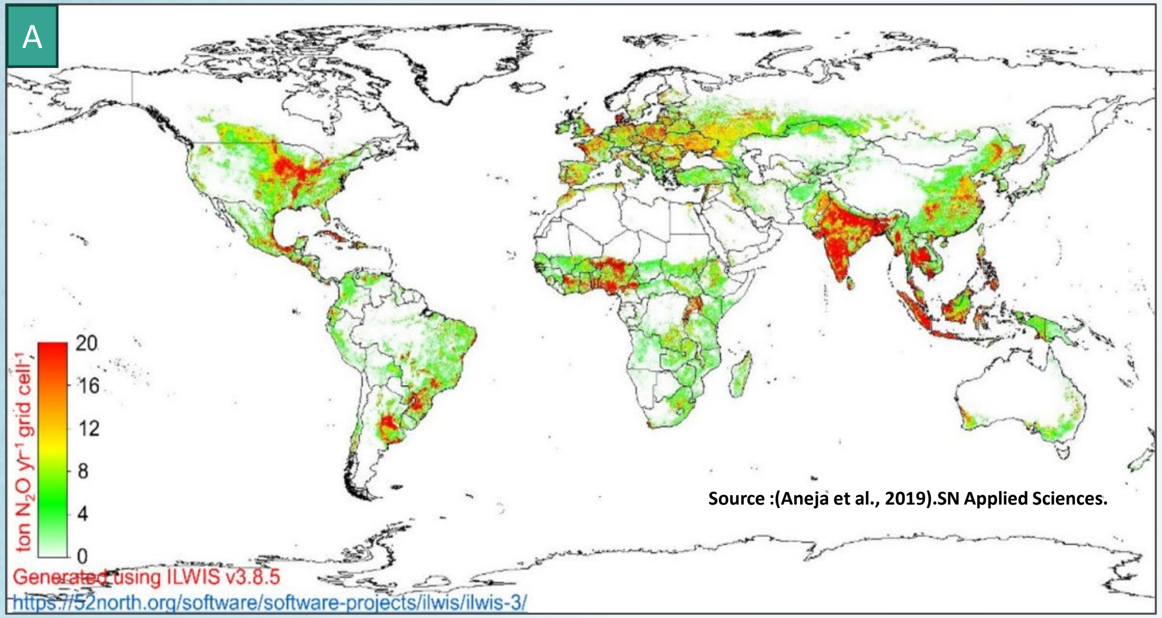
# Background

## ***Processes related to gaseous reactive N products***

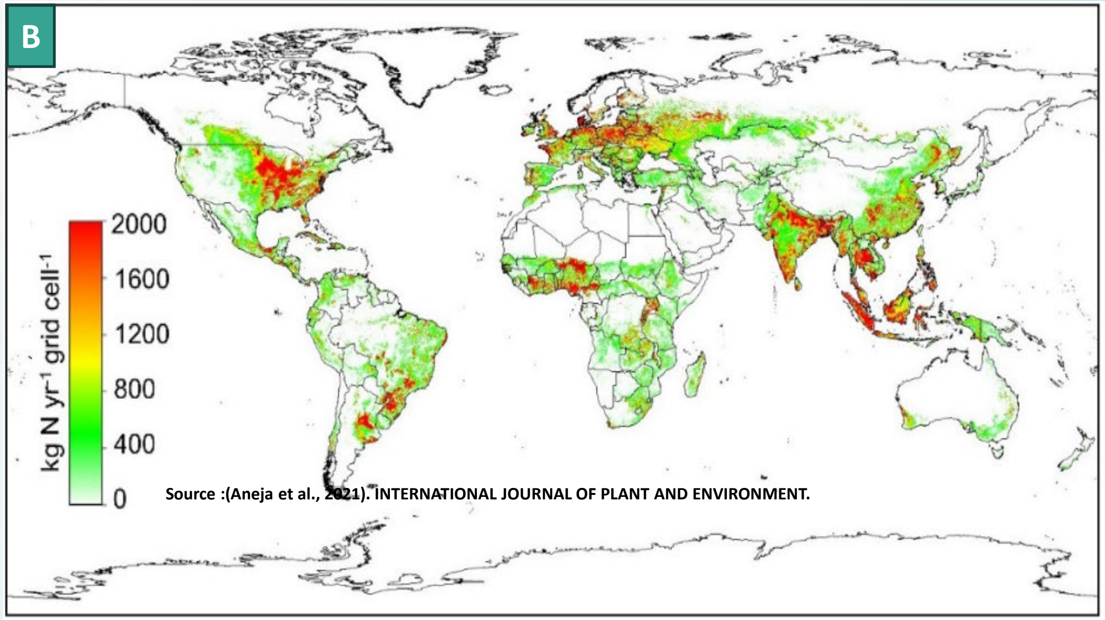



Source: Zhu-Barker et al. Proceedings of the National Academy of Sciences 110 (16), 6328-6333

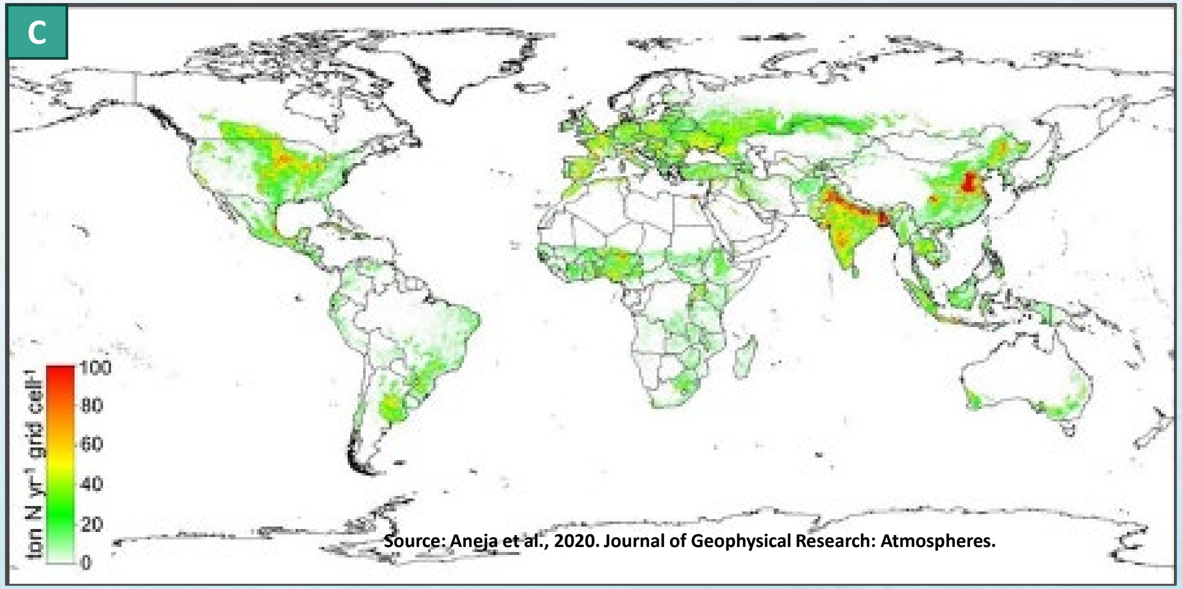
# Atmospheric Reactive Nitrogen Emissions from Global Agricultural Soils




Global Atmospheric $N_2O$ emissions from agricultural sources




Global Atmospheric NOx emissions from agricultural sources




Global Atmospheric $NH_3$ emissions from agricultural sources

# NOx Sources and Reactions of Ozone Formation

NO (nitric oxide) + $NO_2$ (nitrogen dioxide) = NOx

NOx + sunlight (*hv*) are central to the formation of ozone ($O_3$).

$$NO + HO_2 \rightarrow NO_2 + OH$$
$$NO + O_3 \rightarrow NO_2 + O_2$$
$$NO_2 + hv \rightarrow O + NO$$
$$O + O_2 + M \rightarrow O_3 + M$$

Reactions of NOx in the atmosphere lead to nitric acid and fine particulate ($PM_{2.5}$) nitrate.

Sources of NOx:
- Nitrification by soil microbes (denitrification minor source)
- Fuel combustion
- Biomass burning
- Lightning

HONO, the gaseous form of nitrous acid ($HNO_2$) released from soil, contributes to ozone production.

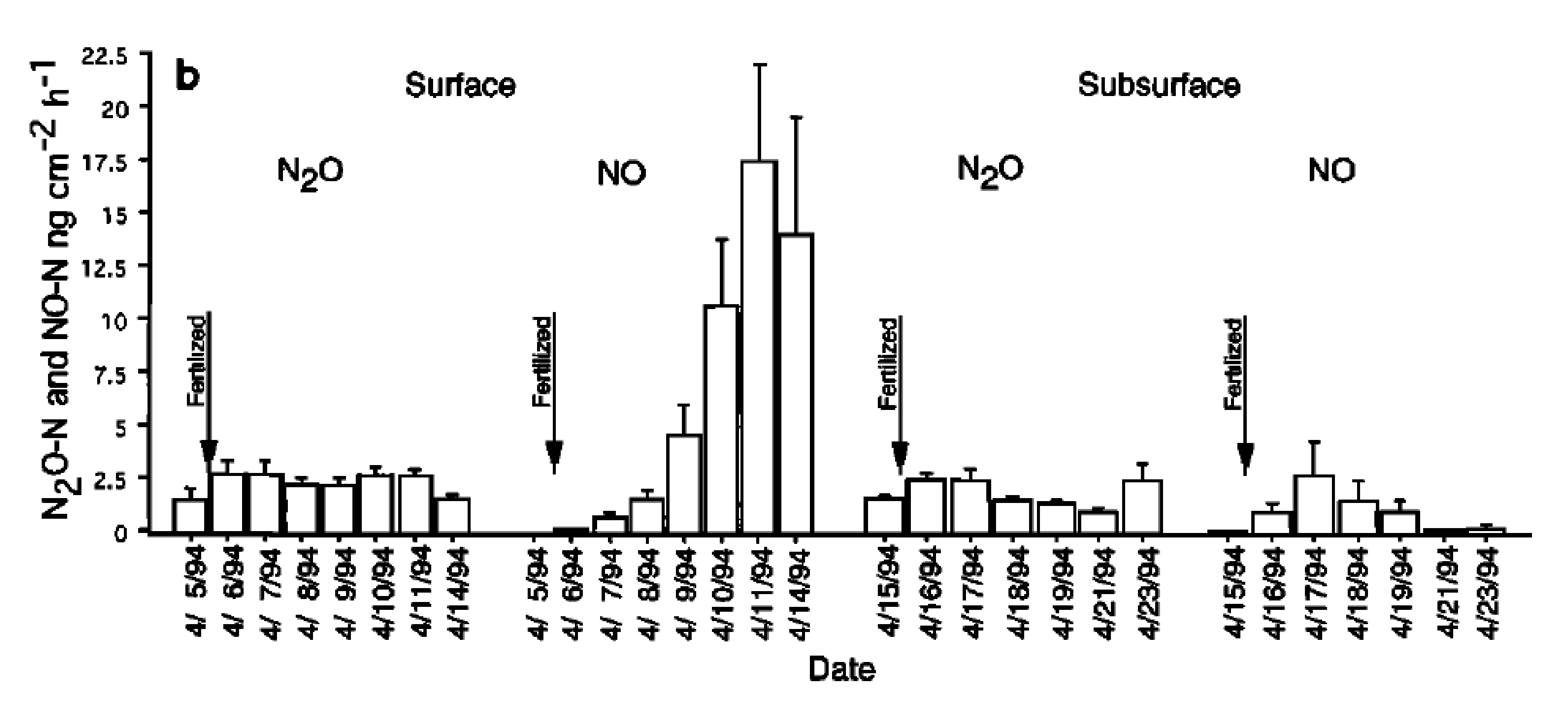
# Driving Factors & Environmental Controls of Soil NOx Emissions

| | |
|---|---|
| $NH_4^+$ availability: | Substrate for nitrification close to the soil surface (top few cm's). $NH_4^+$ availability decreases with increasing time since nitrogen fertilization.<br>NO from denitrification is rarely emitted from soil. |
| Soil Temperature: | Exponential rise of NO emissions between 15 - 35°C.<br>Increasing NO emissions up to 40°C have been observed and other temperature functions have been proposed. |
| Soil Moisture: | Must be sufficient for nitrification<br>High soil water content limits gas transport and increases potential consumption of NO (e.g., nitrous oxide production).<br>Soil wetting after extended dry period causes spikes of NOx. |
| Soil pH: | Low pH drives abiotic production of NO and HONO |

# Driving Factors & Environmental Controls of Soil NOx Emissions

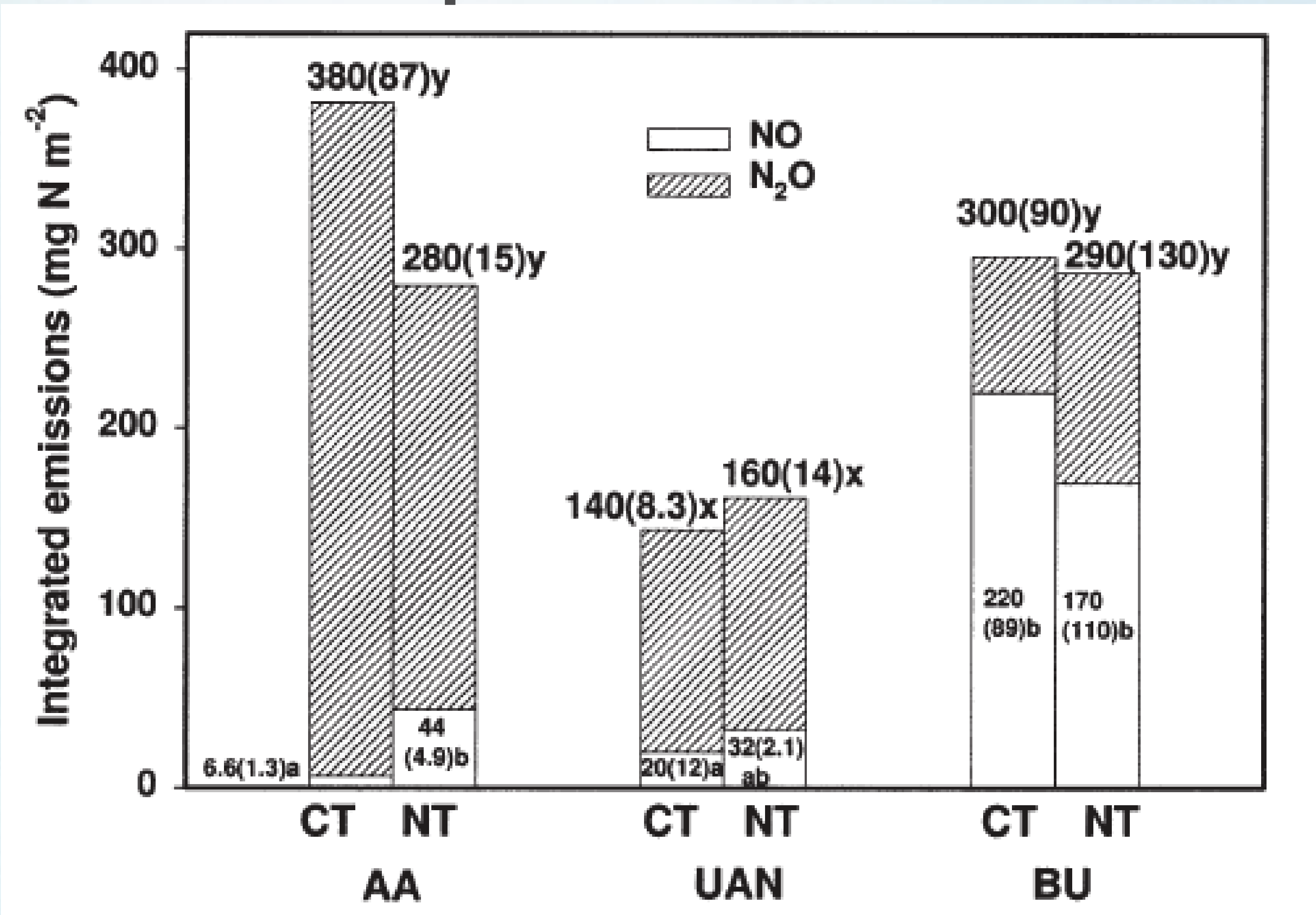
- Physicochemical and biological factors driving NOx production and emissions interact and must all be considered when predicting NOx emissions.
- Driving factors and environmental controls vary at short temporal and spatial scales.
- In agricultural settings, management controls some of the factors:
  - Nitrogen fertilizer placement:
    - Surface application leads to greater NOx emissions than subsurface N fertilizer application.
    - Subsurface drip-irrigation and micro-irrigation systems enable incremental applications of fertilizer N.

# NO emissions in sugar cane in Maui with surface and subsurface application of urea




Matson et al. 1996

# Fertilizer source and placement effects on NO emissions

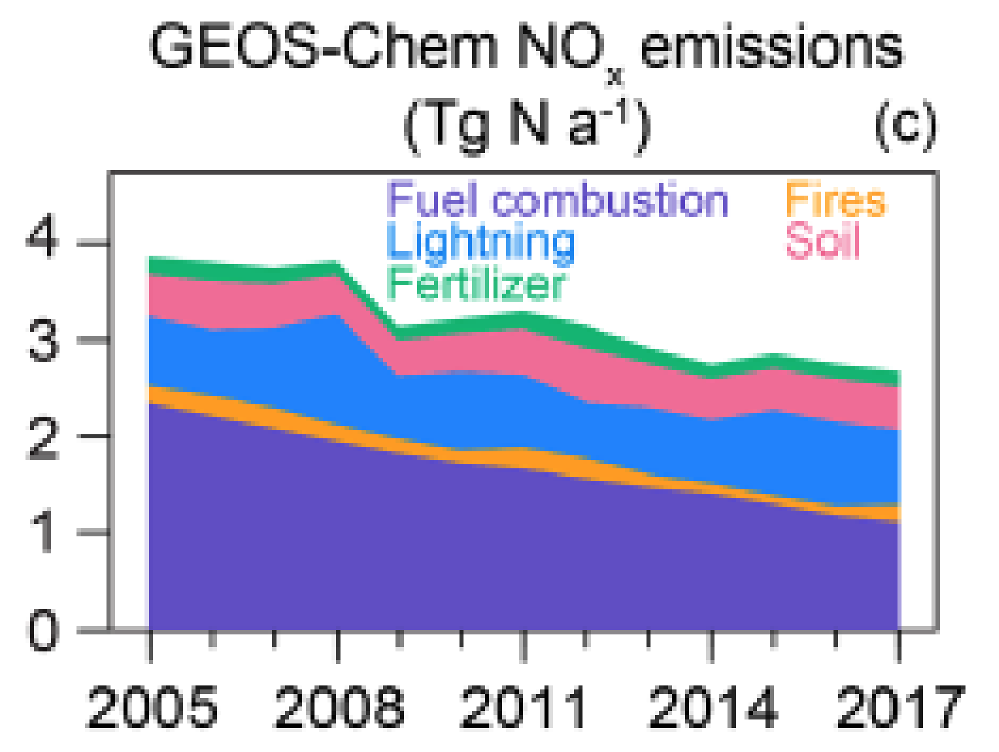



Higher seasonal NO emissions with broadcast urea (BU) than subsurface injected anhydrous ammonia (AA) and urea ammonium-nitrate UAN in rainfed corn in Minnesota (Venterea et al. 2005).

CT=conventional tillage; NT=no tillage.

# Trends of NOx sources since 2005

- NOx emissions from fuel combustion are decreasing
- Relative contribution of soil NOx and other emission sources is getting larger




Modeled emissions for CONUS from 2005-2017 (Silvern et al. 2019)

# Statistical Models Based Observations

- $N_2O$_STAT

$$N_2O\ emission = (\exp[1.34 + 0.03 \times T_{soil} + 0.02 \times SM - 0.35 \times pH_{soil} + 0.0003 \times N\ input + 0.46 \times Fertilizer\ type]) \times \frac{28}{44}$$

- $NH_3$_STAT

$$NH3\ emission = (\exp[-4.6 + 0.02 \times T_{soil} + 0.01 \times SM + 0.09 \times pH_{soil} + 1.2 \times \log(N\ input) + 0.5 \times Fertilizer\ type]) \times \frac{14}{17}$$

- $NO_x$_STAT

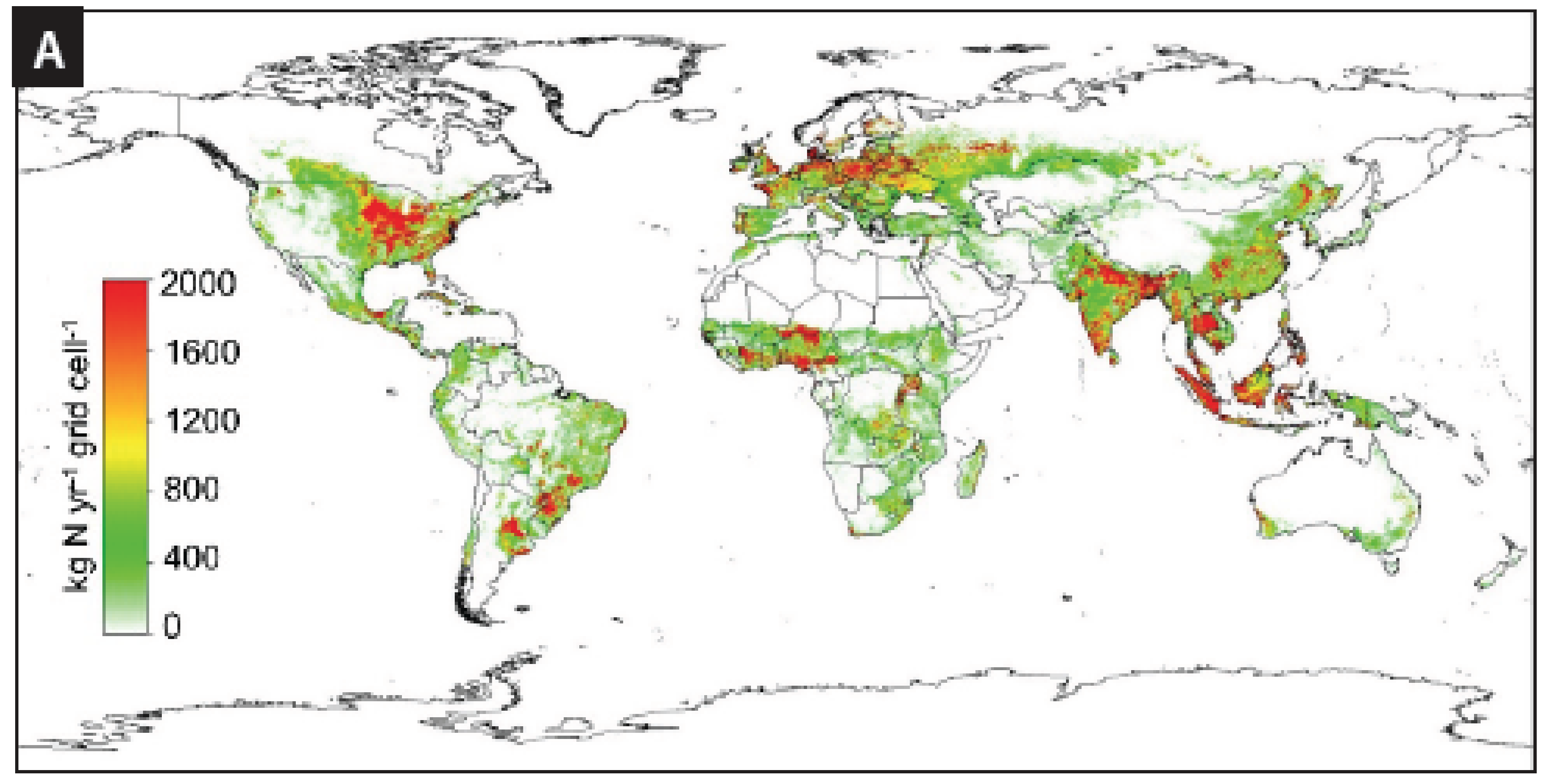
$$NOx\ emission = (\exp[-6.2 + 0.02 \times T_{soil} + 0.02 \times SM - 0.13 \times pH_{soil} + 1.2 \times \log(N\ input) - 0.07 \times Fertilizer\ type]) \times \frac{14}{30}$$

Tsoil refers to soil temperature (°C), SM soil moisture (%), N input is differentiated by synthetic (0) or organic fertilizer (1) and is expressed as kg N $ha^{-1}$ $yr^{-1}$.



The units for predicted emission are kg N $ha^{-1}$ $yr^{-1}$.

# Global soil NOx emissions according to NO-STAT model results (Aneja et al. 2021)



# Soil NOx emission models

Global models:

| | Tg N $yr^{-1}$ | sNOx/total NOx (%) for U.S. | EF (%) | Ref. |
|---|---|---|---|---|
| Y&L | 10.2 | 15-20 | 2.5 | Yienger & Levy 1995 |
| Y&L, top-down constrained (GOME) | 8.9 (+/-8.0) | 22 | 2.5 | Jaegle et al. 2005 |
| BDSNP | 10.7 | 20-33 | 1.5 | Hudman et al. 2012 |
| BDSNP, top-down constrained (OMI) | 12.9 (+/-3.9) | | | Vinken et al. 2014 |

- Semi-mechanistic, empirical models with large uncertainties

- Uncertainties of some global models have been constrained by observations of $NO_2$ columns by satellite-mounted instruments (GOME, OMI, TROPOMI).
- Uncertainties of total NOx emissions affect soil NOx:total NOx.
- The decreasing NOx emissions from fuel combustion increase the soil NOx:total NOx ratio depending on year .

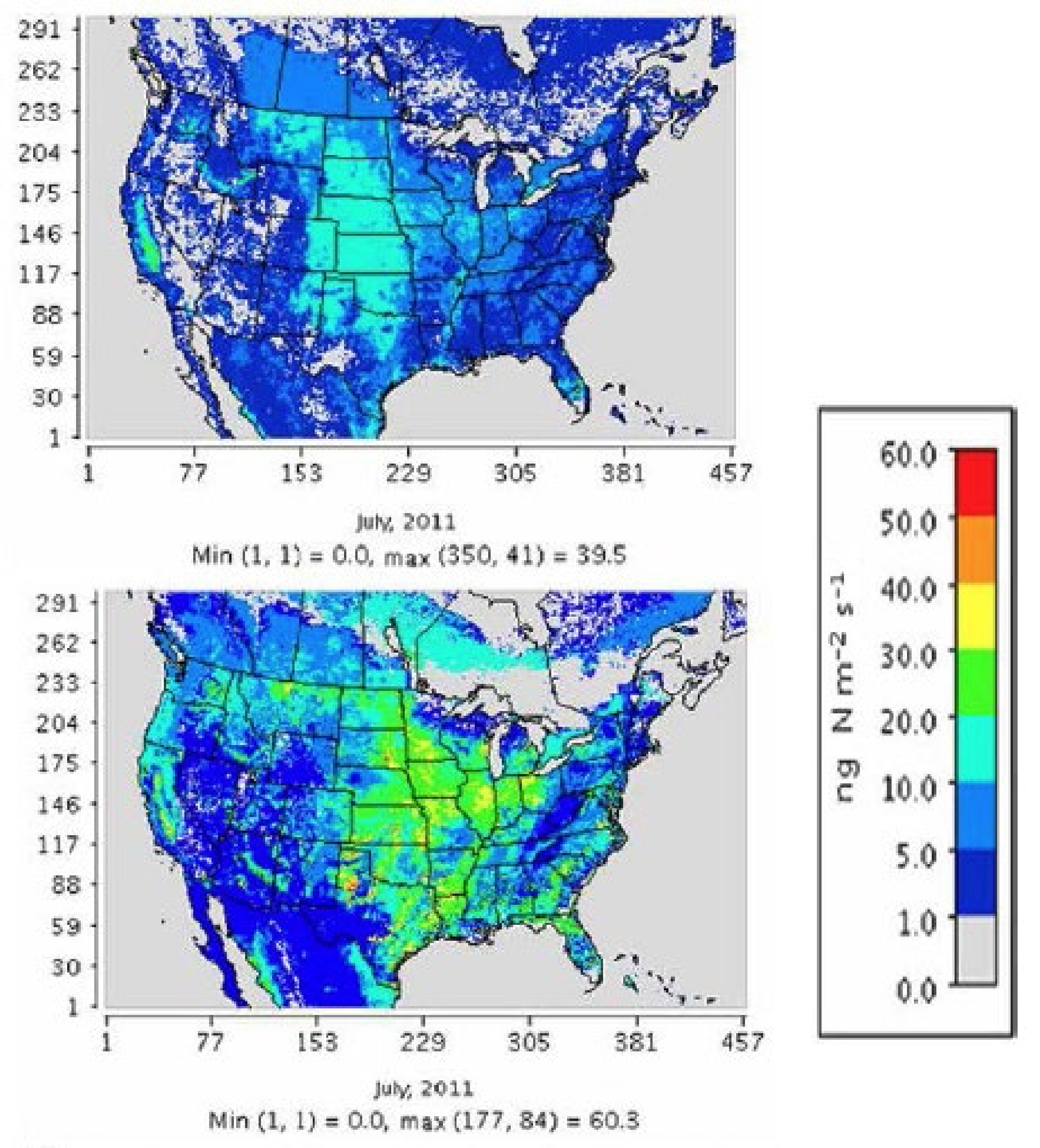
# Soil NOx emission models

Global models for fertilized cropland

| Model | Type | Tg N $yr^{-1}$ | Emission factor | Reference |
|---|---|---|---|---|
| | Statistical | 1.8 (0.36 – 7.3) | 0.55 | Stehfest & Bouwman 2006 |
| NO-STAT | Statistical | 0.67 | 0.45 | Aneja et al. 2021 |
| YL95EMAC | Semi-mechanistic, empirical | 3.13 | 1.0 (+/-2.1) | Steinkamp & Lawrence 2011 |

- Statistical models are based on NOx-fluxes measured in experiments.

# CONUS Soil NOx emissions model comparison




Soil NOx emissions in CONUS for July 2011 simulated by Yienger & Levy (1995) (top) and BDSNP models (bottom) (Rasool et al. 2019).

# Soil NOx emission models for California

| Model | Avg. Mg NOx-N $d^{-1}$ | Emission factor % | Reference |
|---|---|---|---|
| IMAGE | 441 | 15 | Almaraz et al. 2018 |
| BDISNP | 446 | 2.5 | Sha et al. 2021 |
| DNDC | 7.2 | 0.39 | Guo et al. 2020 |

- The IMAGE model simulates NOx emissions based on N surplus (N inputs minus outputs) and an index of WFPS to separate gas species that are potentially emitted. The EF was derived from the mean NOx-N emissions and N fertilizer inputs reported in the publication.
- BDISNP output was reported for the month of July 2018 and included a modified temperature function compared to that of the BDSNP model.
- DNDC is a process-based model that was comprehensively parameterized for all land-cover types and cropping systems including lawns. DNDC informs CARB's emission inventory, the California Emissions Projection Analysis Model (CEPAM).

# Methods & Instrumentation

**Soil NOx emissions:**

- Manual soil cover method with dynamic or static chamber to measure soil-to-atmosphere NO flux by in-situ NOx analyzer : Direct measurement, represents a small footprint, laborious.
- Flux tower data becoming more available for NOx emissions. Continuous above-canopy measurements, greater spatial representation, but more difficult to partition sources of NOx.
- HONO measurement must be measured above ground surface, 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, TEMPO) to retrieve total, stratospheric, and tropospheric $NO_2$ column densities.

# Direct measurements of NOx flux

- Two surveys of NOx flux in California (Matson et al. 1997; Burger & Horwath 2013):
  - >4000 measurements
  - 15 different cropping systems with varying irrigation and fertility management
  - Studies reported seasonal snapshots of NOx emissions and average NOx emissions (ranging from 0.7 - 2.43 g NOx-N $ha^{-1}$ $h^{-1}$).

# Evaluations of recent NOx emission studies in California

- Through our literature review, we identified five recent California studies suggesting that CEPAM values may be too low.
- SMERP evaluation criteria were that modeling results were supported by independent data and statistics. We also considered uncertainties of validation data, such as the uncertainties related to remotely sensed tropospheric $NO_2$ concentrations.
- The results of these studies have high uncertainties but nevertheless indicate significantly higher NOx emissions than reported in the CEPAM inventory.
- All studies involved modeling or were indirect measures requiring additional data to derive the results.

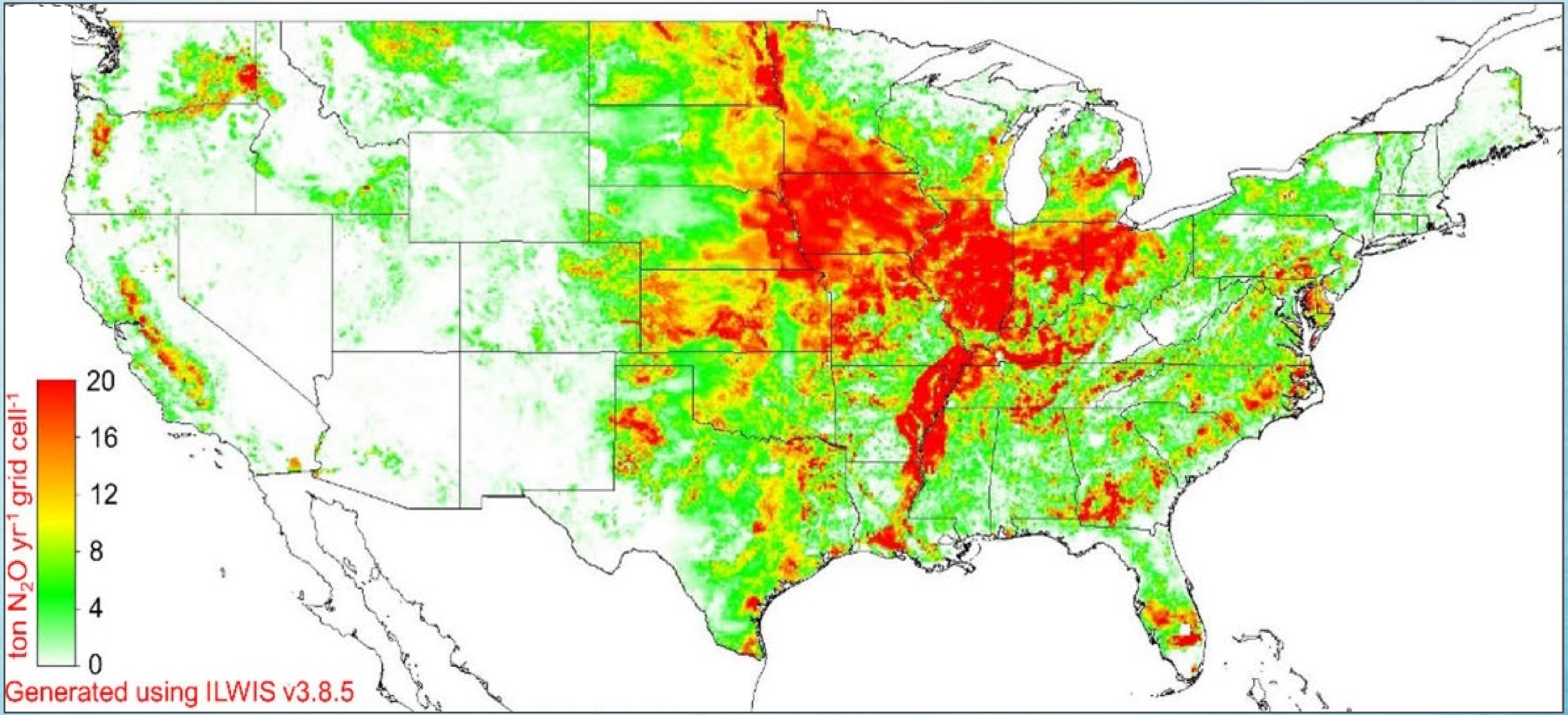
# Evaluations of recent NOx studies in California

- Studies suggesting that CEPAM inventory values may be too low:

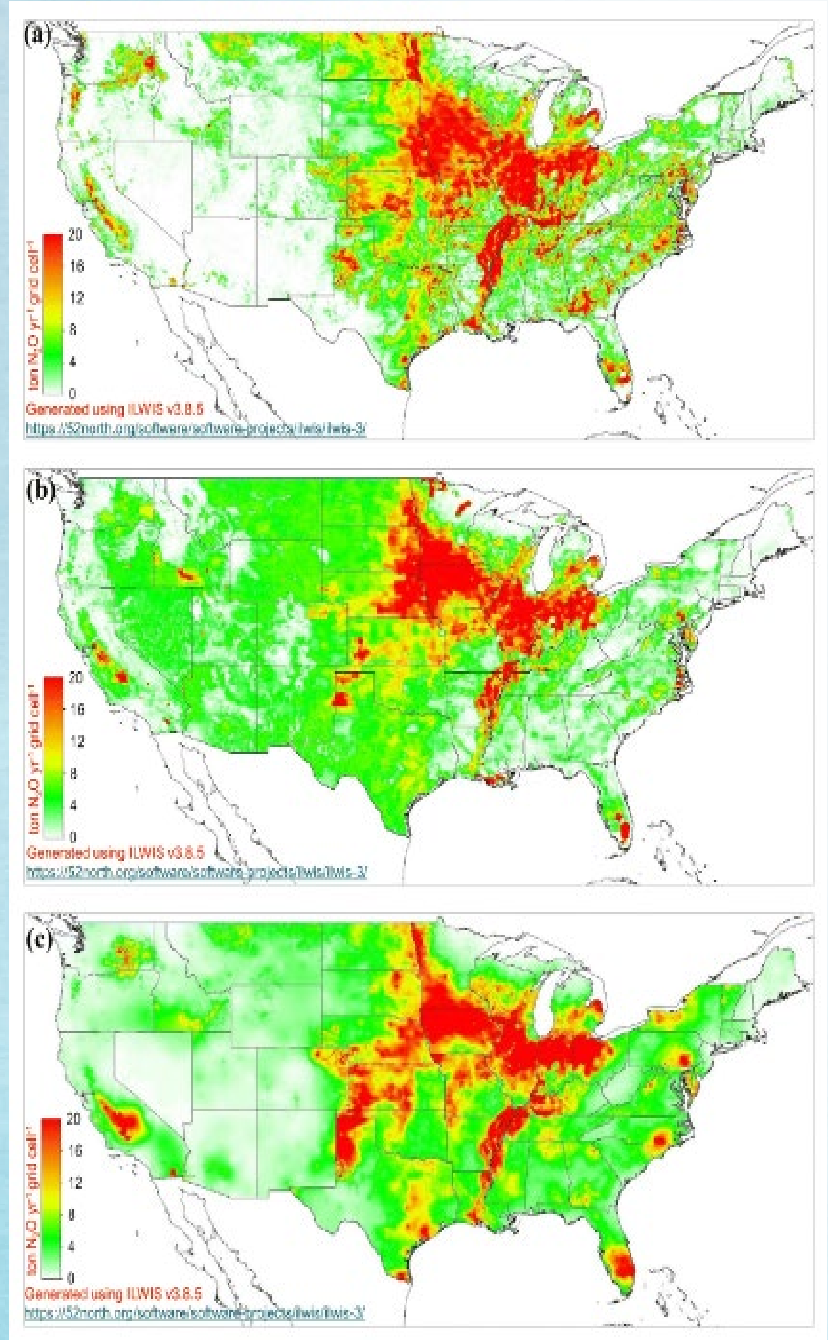
| Ref. | Methods |
|---|---|
| Oikawa et al. 2015 | Modeling of experimental data & OMI (Ozone Monitoring Instrument) observations. |
| Zhu et al. 2023 | Eddy covariance NOx flux by aircraft & desegregation of fluxes according to land cover maps. |
| Trousdell et al. 2019 | Eddy covariance NOx flux by aircraft & inventory of NOx emissions other than those from soils. |
| Chen et al. 2020 | Ground-based measurements of $NO_2$ concentrations at 2 rural locations higher than modeling validated by aircraft measurements. |
| Lieb et al. 2024 | N isotope analysis of monthly air samples to determine the fraction of soil NOx contributed to total NOx. |

# Nitrous oxide ($N_2O$) Emissions from Continental United States Agricultural Soils

**CONUS Atmospheric $N_2O$ emissions from agricultural sources**




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




## $N_2O$ model results with 3 different models

- Estimates of $N_2O$ vary across models with significant consequences for California (Aneja et al. 2019)
- In California, agricultural soils emit on the order of 7 MMT $CO_2$e as $N_2O$ annually, which accounts for almost 60% of the state's total $N_2O$ emissions (Xiang *et al.*, 2013; Tomich *et al.*, 2016) and contributes 2.3% of the total agricultural $N_2O$ emissions in the United States (IPCC, 2013; U.S.EPA, 2024).
- The Central Valley, California's agricultural epicenter, represents a major hotspot for N emissions due to its high value cropping intensity and substantial fertilizer and manure inputs.

# Measurement of $N_2O$ emissions

Several methods exist for $N_2O$ measurements. Continuous sampling can capture hot moments of emissions that can account for over 50% of annual fluxes (Anthony and Silver, 2024).

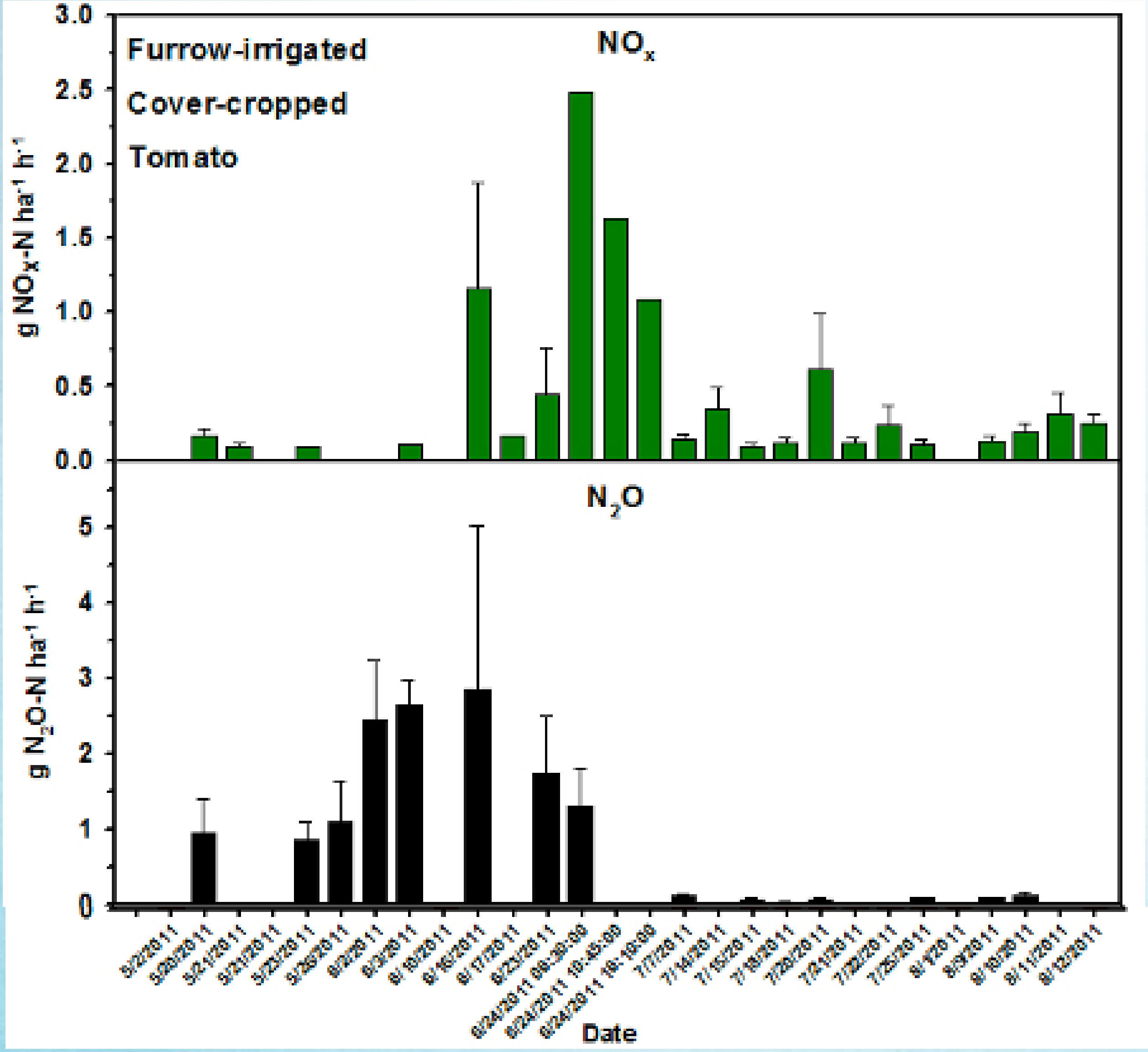
The disadvantage is the cost (often >$100K per CRDS instrument) as well as the limited spatial coverage at the field scale.

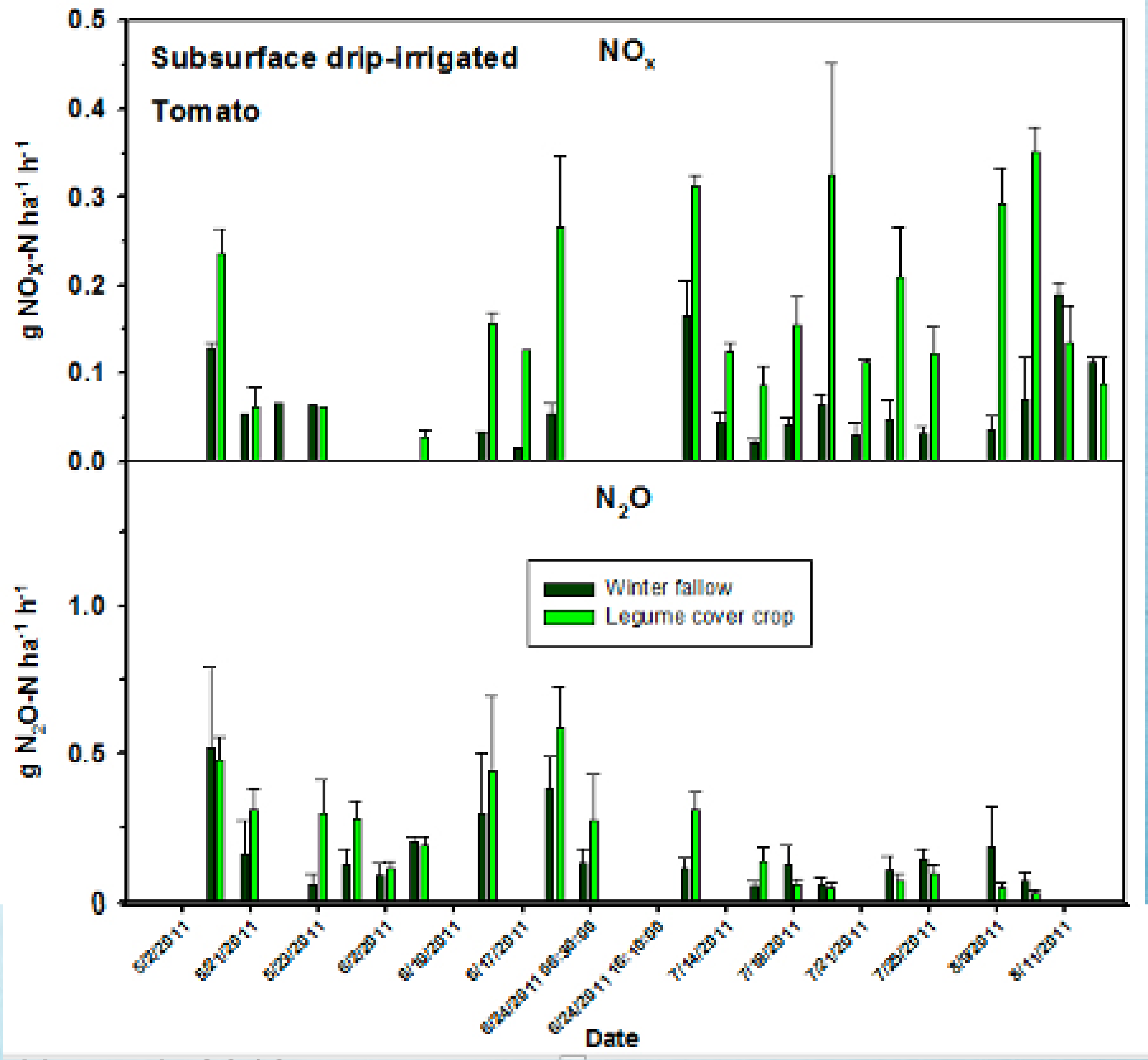
Photo: Brett Sattazahn

Photo: Tyler Anthony

Photo: Camilo Rey

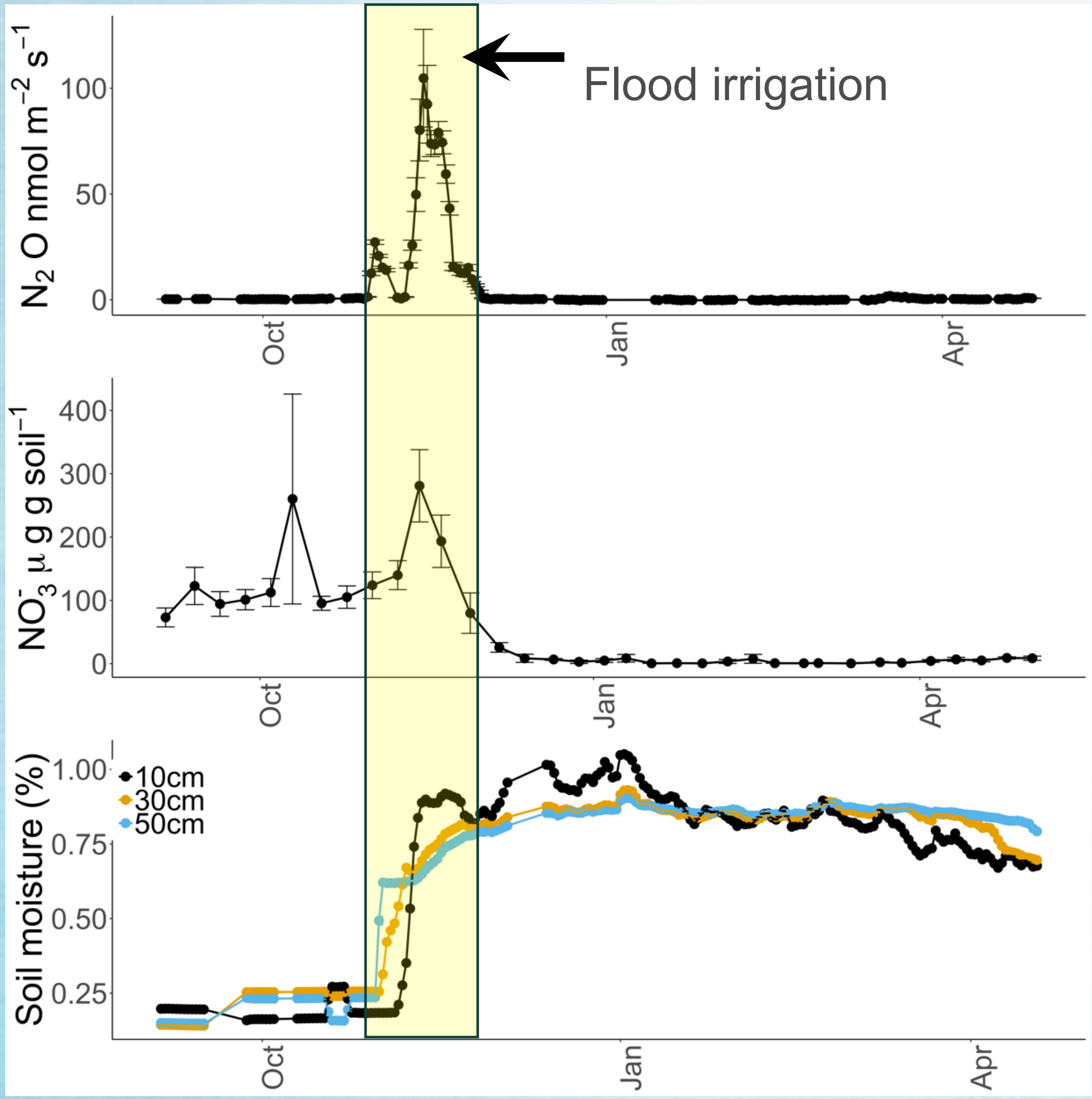
# Greater spikes of NOx and $N_2O$ emissions in furrow-irrigated than subsurface drip-irrigated tomato systems.



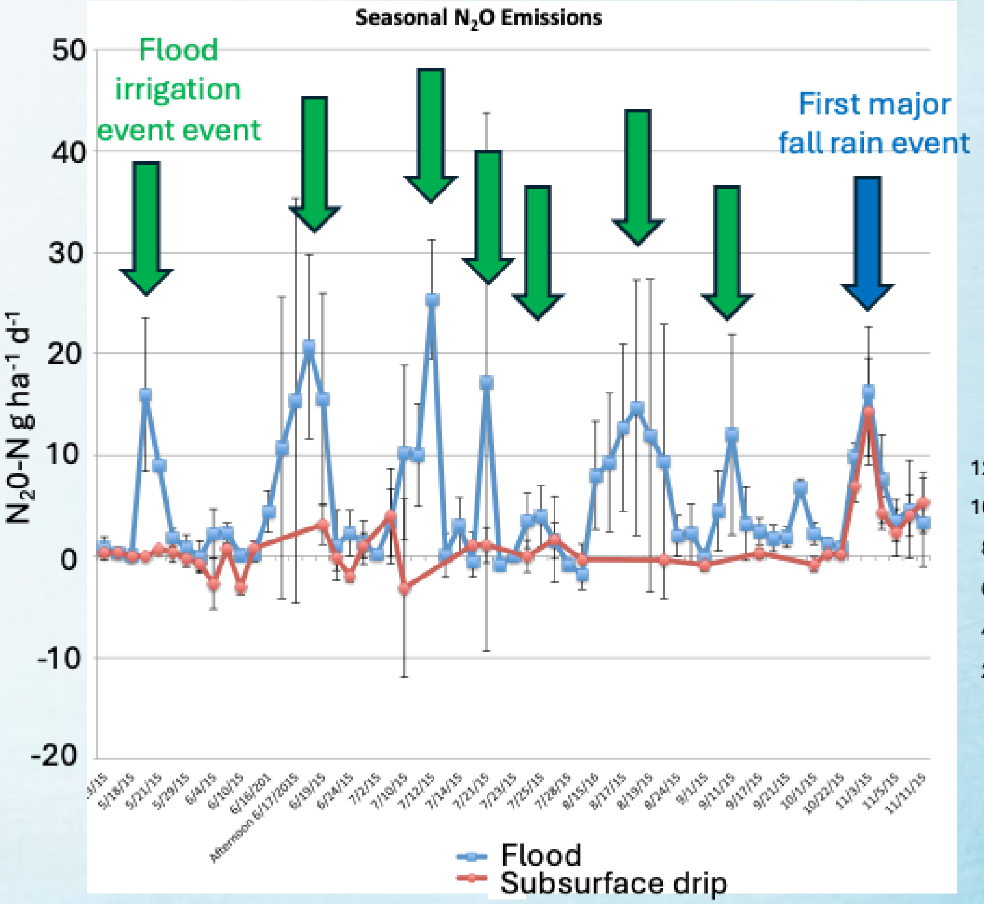



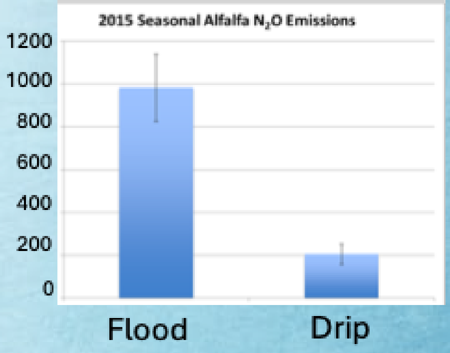

Burger & Horwath 2013

# Flood irrigation stimulates hot moments of $N_2O$ emissions in maize and alfalfa. Subsurface drip irrigation can reduce overall $N_2O$ emissions in croplands.



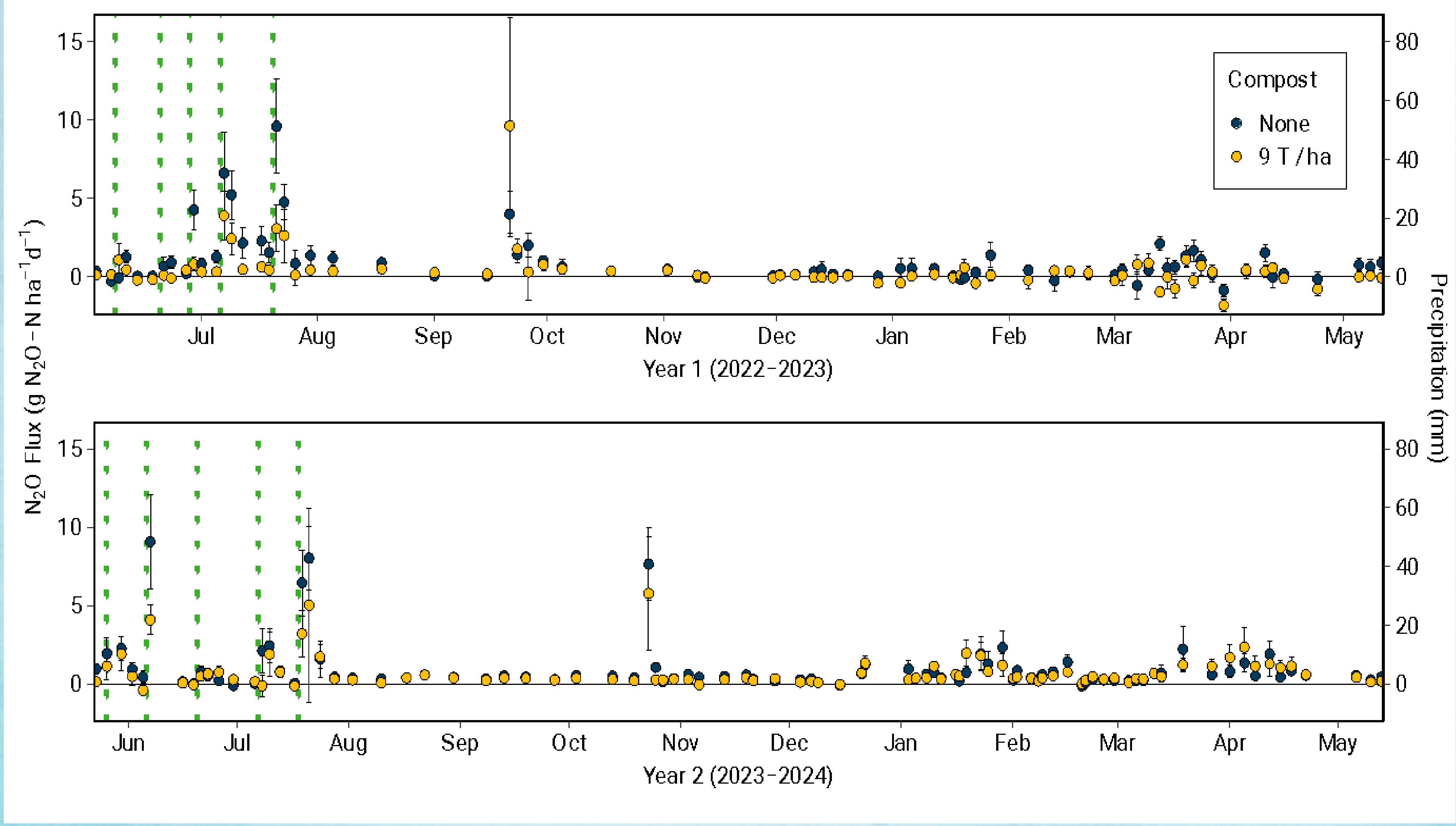

Anthony and Silver 2021




Byrnes et al. 2015

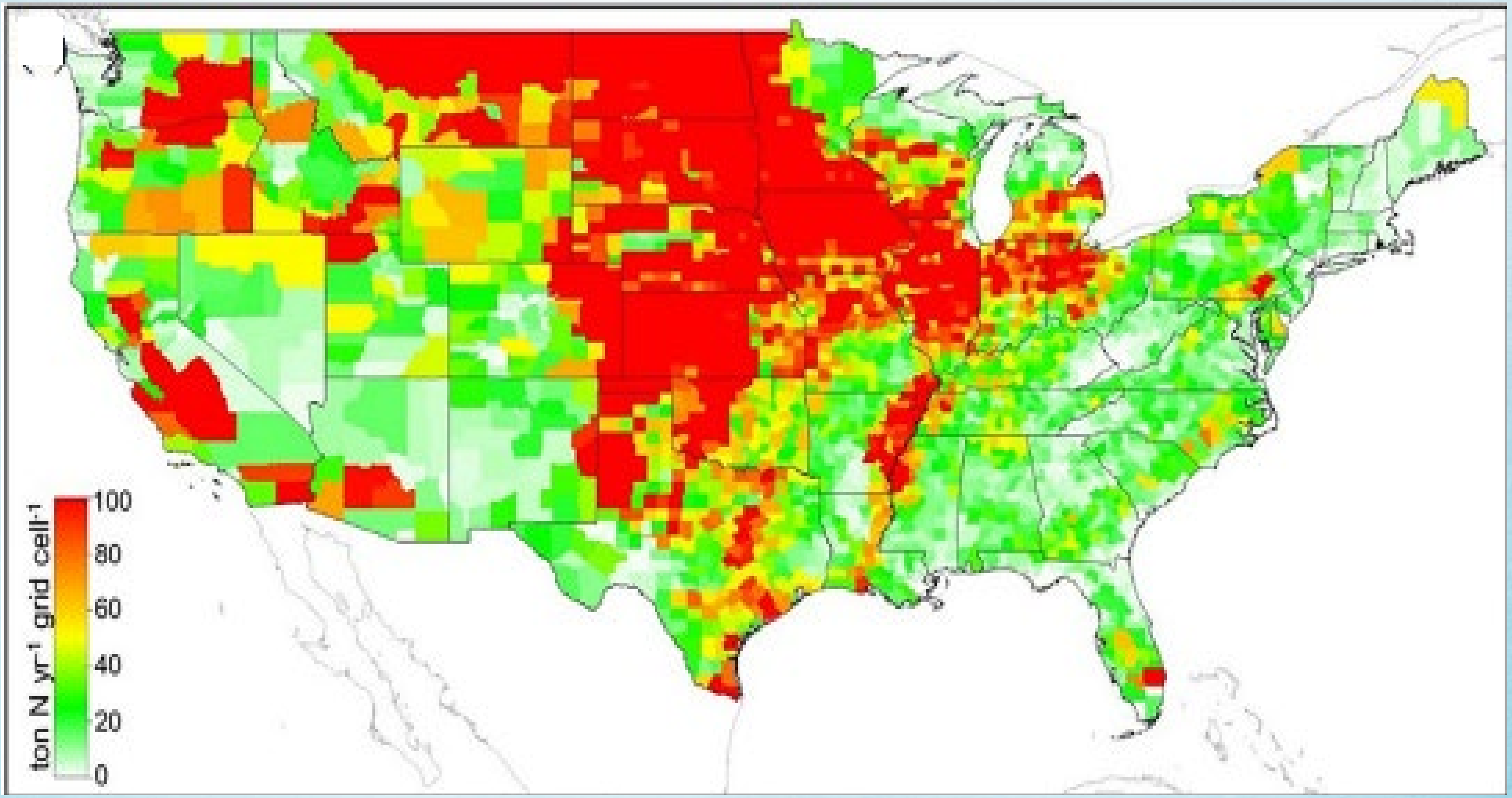
# Compost effects on $N_2O$ emissions




While inorganic fertilizer is known to increase $N_2O$ emissions, compost does not appear to increase emissions and can decrease emissions in cropping systems and orchards.

# Ammonia ($NH_3$) Emissions from Continental United States Agricultural Soils

**CONUS Atmospheric $NH_3$ emissions from agricultural sources**




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

- Ammonia emissions vary across inventories, posing challenges for accurately quantifying agricultural N losses and informing mitigation strategies (Aneja et al., 2020).

- In California, agriculture is the dominant source of $NH_3$ emissions, with the Central Valley contributing disproportionately due to intensive cropping and concentrated livestock operations (Vechi et al., 2023; Krauter et al., 2002).

- Ammonia volatilization from soils is highly variable and influenced by soil pH, moisture, temperature, and N management, complicating measurement and mitigation efforts (Sutton et al., 2009; Rochette et al., 2013; Scotto di Perta et al., 2020).

# Recommendations

- SMERP recommends obtaining **additional data** on soil NOx emissions and ancillary data to improve model parameterizations and allow for robust validation of model outputs. Currently available data are temporally too sparse to validate DNDC model outputs.
- Future assessments of soil NOx emissions must take advantage of **multiple measurement and monitoring approaches in concert** to address the uncertainties of soil NOx emissions estimates.

# Recommendations

- Need for continuous, or at a minimum, frequent NOx flux measurements:
  - Chamber-based methods yield direct measurements NO flux; must be made with sufficient frequency (daily to weekly) to provide robust estimates of cumulative emissions for the entire season or year.
    - To mitigate the limitation of the small surface area a chamber covers, chamber locations must be carefully selected to represent the different moisture regimes within a study site.
    - The location of N fertilizer placement must also be considered when chamber locations are selected.
  - Flux gradient  or eddy covariance methods yield continuous NOx data, capture ‘hot moments’ of emissions, cover larger areas, and measure above-canopy flux, but separation of sources more difficult.

# Recommendations

- To cope with the uncertainty of NOx emission predictions, installing **additional ambient $NO_2$ monitoring sites** in rural locations is recommended.
  - Almost all current ground-based air quality monitoring sites are in urban or near-highway locations.
  - Integrated measure of the effects of soil NOx emissions on air quality, provided the inventories of the other ambient NOx sources are accurate .
- To validate estimates of total NOx and to locate areas with high concentrations of $NO_2$, continued use of **remotely sensed $NO_2$ column data** by satellite-mounted instruments is recommended.
  - The 2023 launched TEMPO geostationary satellite provides hourly data at the spatial resolution of 2 km x 4.75 km.

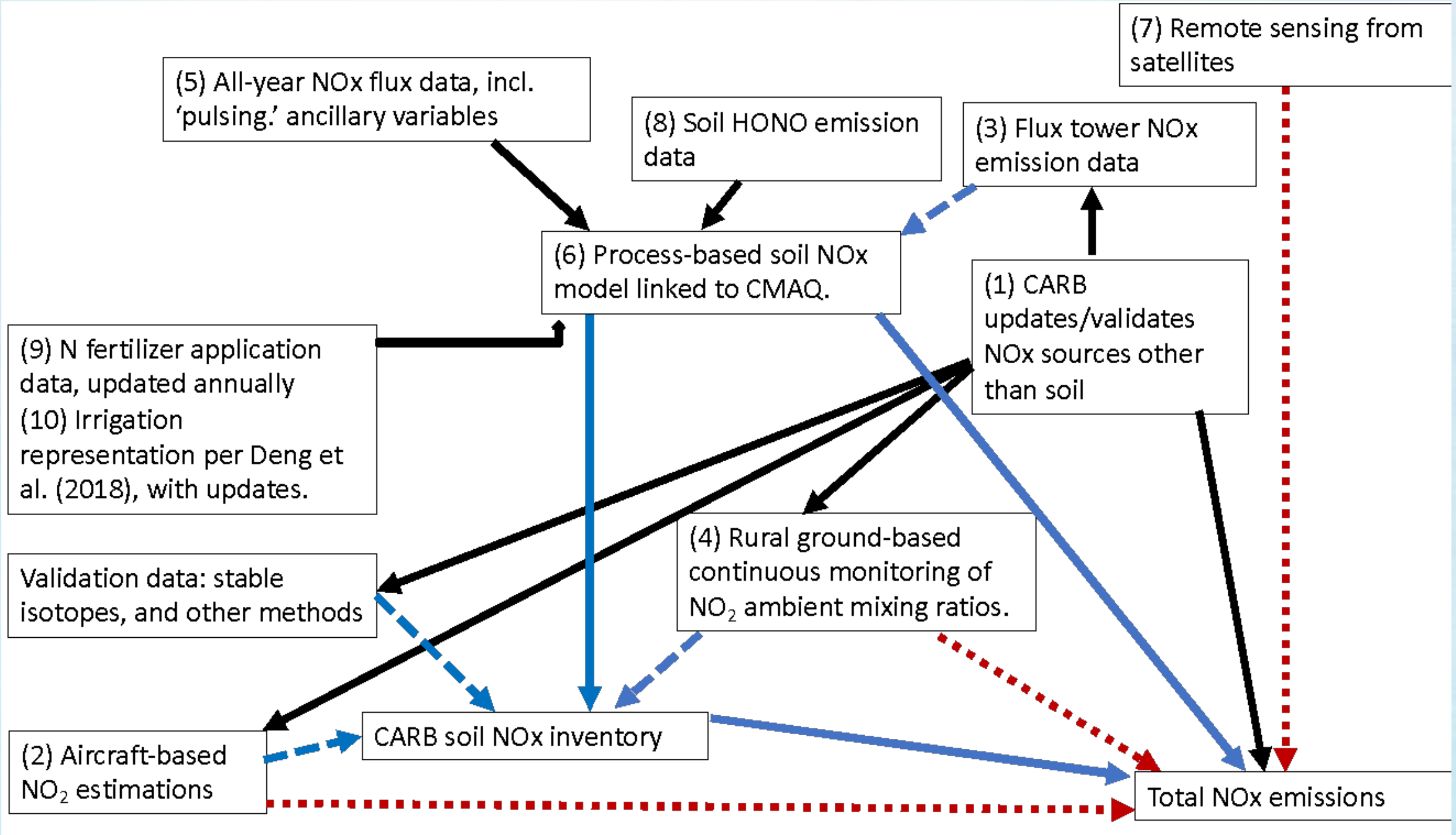
# Recommendations

- To better parameterize model inputs, maintaining a regularly updated database of **N fertilizer use and application times** is recommended.
  - California Water Boards collect fertilizer use data aggregated by crop and region via the Irrigated Lands Regulatory Program.
  - Information on N fertilizer application timings may be obtained from UC Cooperative Extension Specialists, county Agricultural Commissioners.

# Recommendations

- Under-researched topics in California:
  - HONO releases hydroxyl radicals and increases ozone levels.
    - Ammoniacal fertilizer can be a strong HONO source.
  - Pulsing, the rapid NOx emission response to wetting soils that have been dry for an extended time, can contribute up to 25% to soil annual NOx emissions.
    - The importance of pulsing in California's cropland has not been demonstrated.
  - Ammonia emissions
    - Instrumentation for continuous measurements is becoming available.
    - Research should focus on soils amended with manure, digestate, nitrification and urease inhibitors, and soils under subsurface drip irrigation.
  - Continuous measurement of $N_2O$ flux to capture hot moments and improve inventories.
    - Instrumentation for continuous measurements is widely available.
    - Studies focusing on organic and N-rich amendments are needed.

# Additional data sources to inform CARB's soil NOx inventory




Model inputs

Model outputs

Soil NOx emission data require input of NOx sources other than soil

$NO_2$ density data must be converted to NOx emissions by modeling


Thank you!