Scientific Evaluation of Nitrogenous Emissions from Soils

FINAL REPORT

California Air Resources Board, Contract No. 23RD017

Prepared for: California Air Resources Board

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May 28, 2025

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Acronyms

Anammox – Anaerobic ammonium oxidation

BDSNP - Berkeley Dalhousie Nitric Oxide parameterization

BDISNP - Berkeley Dalhousie Iowa Nitric Oxide Parameterization

BEIS - Biogenic emission inventory system

BELD - Biogenic emissions landcover database

C – Carbon

CARB - California Air Resources Board

CASA - Carnegie-Ames-Stanford Biosphere

CDWR – California Department of Water Resources

CEPAM - California emissions projection analysis model

CMAQ - Community multiscale air quality

CO₂ – Carbon dioxide

Comammox – Complete ammonia oxidation

CONUS - Continental United States

CRF - Canopy reduction factor

N – Ratio of ¹⁵N:(¹⁵N+¹⁴N) atoms

DISCOVER-AQ – Deriving information on surface conditions from column and vertically resolved observations relevant to air quality

DNDC – DeNitrification-DeComposition Model

DNRA - Dissimilatory nitrate reduction to ammonium

EDGAR - Emissions Database for Global Atmospheric Research

EF - Emission factor

EPIC - Environmental Policy Integrated Climate

Feammox – Iron-coupled ammonium oxidation

FAO - Food and Agriculture Organization

FIE - Fertilizer-induced emission

Gg – Giga gram (1x10⁹ grams)

GOME – Global ozone monitoring experiment

GWP – Global warming potential

- HNO₃ Nitric acid
- HNO2 Nitrous acid
- HO₂ Hydroperoxyl radicals
- HONO gaseous form of nitrous acid (HNO₂)
- hv light energy, visible light
- IBBCEAS Broadband Cavity Enhanced Absorption Spectroscopy
- LOPAP Long path absorption photometer
- M Non-reacting molecule, absorbs reaction energy
- MEGAN Model of emissions of gases and aerosols from nature
- Mg Mega gram $(1x10^{6} \text{ grams})$, one metric tonneNH₃ Ammonia
- N2 Atmospheric nitrogen, dinitrogen
- NH₃ Ammonia
- $\rm NH_4^+$ Ammonium
- NO₃ Nitrogen trioxide radical
- NO₃⁻ Nitrate
- NO Nitric oxide
- NO₂ Nitrogen dioxide
- N₂O Nitrous oxide
- NH₂OH Hydroxylamine
- NO_x Sum of nitric oxide (NO) plus nitrogen dioxide (NO₂)
- $O_2 Oxygen$
- O₃ Ozone
- OH Hydroxyl radical
- OMI Ozone monitoring instrument
- IMAGE -- Integrated Model for the Assessment of Global Environment
- NASA National aeronautics and space administration
- NEI National emissions inventory
- U.S. EPA United States Environmental Protection Agency
- pH Logarithmic scale used to specify acidity or basicity of aqueous solutions
- PM_{2.5} Particulate matter of diameter less than 2.5 micrometer

REA – Relaxed eddy accumulation

TEMPO – Tropospheric emissions monitoring pollution

- $Tg Tera gram (1x10^{12} grams)$
- VOC Volatile organic compound
- WFPS Ratio of volumetric soil water content to total porosity
- WRF-Chem Atmospheric Chemistry Observations & Modeling

Acknowledgements

We would like to thank Dr. Bash for providing soil NO emissions for the EPA NEI: Bash, Jessie, 2024. "Draft soil NO white paper" and Dr. John K. Moore for helpful discussions on the evaluations of statistics in the reviewed literature.

This report was submitted in fulfillment of CARB Contract No. 23RD017 Scientific Evaluation of Nitrogenous Emissions from Soils by the University of California, Davis, under the sponsorship of the California Air Resources Board. Work was completed as of May 28, 2025

Executive Summary

The objective of this project was to evaluate the current scientific literature, databases, and published reports on nitrogenous (i.e., reactive nitrogen) emissions, in particular nitric oxide (NO), ammonia (NH₃), and nitrous oxide (N₂O) from soils in California with the goal of improving the accuracy of the California Air Resources Board inventory of these gases. Nitric oxide (NO) and nitrogen dioxide (NO₂) are closely coupled in reactions taking place in the atmosphere; NO_x represents the sum of NO and NO₂. NO_x is a precursor of ozone formation in the troposphere, and NH₃ and NO_x are precursors of airborne ammonium nitrate, a common type of fine particulate matter (PM_{2.5}) air quality constituent of concern in the Central Valley. Besides soils, fuel combustion, biomass burning, and lightning are also major sources of NO_x. During the last two decades, great strides have been made in lowering NO_x from mobile sources in California and the U.S. as a whole. Therefore, sources of NO_x other than fuel combustion, which now dominates global NO_x production, are becoming relatively more important. N₂O is a potent greenhouse gas.

Soil production and emissions of NO_x are dynamic processes controlled by physicochemical and biological factors, such as soil moisture, temperature, ammonium availability, soil pH, soil texture, and microbial activity. These factors can vary greatly at short temporal and spatial scales. In California's agricultural settings, management controls some of these factors. For example, subsurface drip-irrigation combined with fertigation has been shown to lower both N₂O and NO_x emissions as nitrogen fertilizer can be applied incrementally with the irrigation water according to crop needs at the depth where most roots are located.

Estimating the magnitude of soil NO_x emissions, both globally and regionally, has been fraught with uncertainty. Global annual estimates of soil NO_x emissions range from 5.5 to 23.6 Tg per year; in the San Joaquin Valley, recently published values of NO_x emissions from soils differ by an order of magnitude. Recent advances in measurement techniques and new datasets provide intriguing evidence of the role of soils in NO_x emissions in California. However, the role of soil NO_x emissions as tropospheric ozone precursors in California has not been well established.

We summarized the salient features of the most widely implemented soil NO_x models developed in the last 30 years. Most models have empirical and mechanistic, or process-based, components. All models include algorithms that predict NO_x emissions utilizing the exponential relationship between soil temperature and NO_x flux. While empirically derived biome-specific NO_x emission rates generated from field measurements were used in some global and regional models, more recently, process-based mechanisms have been built into simulation models. For example, the Community Multiscale Air Quality (CMAQ) model parameterizations utilize the widely tested biogeochemical sub-model DayCent to represent nitrogen transformations and NO_x emissions based on Environmental Policy Integrated Climate (EPIC) model inputs. Modeling outputs must be validated with independent measurements. Validation of global and regional soil nitrogen gas emissions models has not been extensive. Modeled tropospheric concentrations of NO₂ have been compared with tropospheric NO₂ density observed from satellite-mounted instruments. The remotely sensed data includes NO_x from sources other than soil, and there are uncertainties associated with estimates of non-soil NO_x. Furthermore, the uncertainty of the remotely sensed observations, related to the conversion of spectral data to NOx abundance in the troposphere, must also be considered.

Studies on how to reconcile remotely sensed top-down and bottom-up estimates from NO_x inventories are discussed.

We evaluated the most recent studies estimating soil NO_x emissions in California, including various methods such as flux chamber measurements, eddy covariance methods by aircraft, a stable isotope study, and modeling. Our criteria for evaluating estimates of NO_x emissions were that results had to be supported by independent data and statistics. Five studies described in this report suggested that soil NO_x emissions listed in CARB's *California Emissions Projection Analysis (CEPAM)* inventory may be too low based on our criteria. Currently, *DeNitrification DeComposition* (DNDC) modeling outcomes inform CEPAM. The parameterization of DNDC was comprehensive covering all major land-use types that potentially emit NO_x from soil, but the data sets of the measured fluxes used as model validation were temporally too sparse to allow estimates of seasonal or annual emissions for verification of the modeling results. We therefore recommend that CARB obtain additional NO_x emissions data. To cope with the temporal and spatial variability of NO_x emissions and the uncertainty of modeling results, future assessments of NO_x emissions must take advantage of multiple measurement approaches in concert. Our recommendations are as follows:

- NO flux measurements providing reliable estimates of cumulative seasonal soil NO_x emissions throughout the entire year are needed. Chamber-based methods yield direct measurements of NO. Such studies can validate modeling assumptions and outcomes by helping to identify driving mechanisms. The limitation of flux chamber methods is the small area of soil surface that each chamber covers. This limitation must be mitigated through careful chamber location selection and replication within study sites. It is also possible to measure NO_x continuously using newly available laser instrumentation or a flux gradient or eddy covariance method. The advantages of these methods are the ability to capture hot moments of emissions; towers yield greater spatial representation than flux chamber methods, and the ability to measure above-canopy NO_x flux emissions.
- We recommend the installation of additional ambient air quality monitoring stations in rural locations, ideally surrounded by agricultural fields, since almost all current air-pollutant monitoring sites are in urban or near-highway locations. The continuous monitoring of ground-level nitrogen dioxide (NO₂) and ozone (O₃) will provide direct information on the effects of soil NO_x emissions if the inventory of the other NO_x sources is accurate.
- Continued use of remotely sensed data of NO₂ collected by satellites to validate estimates of total NO_x is recommended. This approach also requires accurate estimates of NO_x from sources other than soil. With the launching of the new satellite platform, TEMPO, with greater spatial and temporal resolutions, the opportunities to locate hot spots of emission and validate modeling are likely growing.
- Create a regularly updated database of N fertilizer use by crop and region. Much information is collected by the State Water Boards for the Irrigated Lands Regulatory Program, and additionally, information on the timing of fertilizer applications may be obtained in collaboration with UC Cooperative Extension Specialists and county Agricultural Commissioners. Having accurate information of N fertilizer applications, especially the timing of applications, will improve the parameterization of NO_x models as the time of fertilizer applications is a critical variable for predicting NO_x flux.

- Conduct more research on emissions of gaseous nitrous acid (HONO) above the soil. HONO contributes to tropospheric ozone. Measurements in China have shown strong HONO emissions from agricultural fields after the application of nitrogen fertilizer. HONO is not captured with traditional flux chamber measurements.
- More continuous, soil-centric measurements are needed for NH₃ and N₂O as new approaches and instrumentation are becoming available. Recent work on N₂O highlighted the need for continuous measurements to reduce the risk of significant underestimation of total nitrogen emissions due to the episodic nature of fluxes.
- Work focusing on soils amended with manure and other soil amendments (compost, biochar, rock dust, digestate) is a research priority, especially to understand their effects on the production of NO_x, N₂O, NH₃, and HONO under different cropping systems, rangeland, and environmental conditions. Few comprehensive datasets are available for NH₃ fluxes from California's working lands, but the widespread use of livestock manures and the growing use of anaerobic digestate are likely to be important sources. In addition, the role of irrigation practices, including micro-irrigation, fertigation, surface irrigation, and flooding should be evaluated in relation to nitrogen availability and seasonal emission patterns. These practices interact with fertilize type, application frequency, and soil properties (e.g., organic carbon content, texture, pH) in ways that remain poorly understood and could significantly affect nitrogenous emissions. Addressing these knowledge gaps will improve modeling accuracy and inform state's strategies of mitigating agricultural air pollution.

1. Introduction

The objective of this report is to evaluate the current state of the science on nitrogenous (e.g., NO_x (NO, NO₂), N₂O, NH₃) emissions from soils in California, emphasizing agriculture where nitrogen fertilizers and organic nitrogen (N) sources and materials are applied. The Subject Matter Expert Review Panel (SMERP) on nitrogenous emissions from soils was tasked to comprehensively review available scientific literature, pertinent databases, and emission estimation methodologies that improve the understanding of the accuracies and uncertainties associated with nitrogenous emission predictions for soils. The SMERP was assembled by the California Air Resources Board (CARB) (based on a national search) to provide guidance and information so the agency can provide the best scientific evidence on nitrogenous emissions from soils. The panel (authors) members are: William R. Horwath, UC Davis; Whendee L. Silver, UC Berkeley; Xia Zhu-Barker, University of Wisconsin-Madison; Viney P. Aneja, North Carolina State University; and Martin Burger, California Department of Food and Agriculture (formerly).

CARB has included nitrogenous emissions from soils in regional air quality modeling for decades and has more recently adopted the DeNitrification-DeComposition biogeochemical (DNDC) model to assess the predictive capabilities of the Community Multiscale Air Quality (CMAQ) model. A publication (Almaraz et al., 2018) suggested opportunities for NOx emission reduction in California's Central Valley by revealing potentially overlooked NO_x emissions from soils, which were estimated to be 24 kg N ha⁻¹y⁻¹ in California's San Joaquin Valley (SJV). However, Guo et al., (2020) suggested that NO_x emissions from soils do not significantly contribute to California's NO_x budget. In 2023, Zhu et al. published a study highlighting the importance of NO_x emissions from soils in the SJV based on aircraft-based measurements, which reported 0.79 mg m⁻ 2 h⁻¹ over cropland during the peak soil NO_x flux season. Another study that used stable N isotope dilution methodology suggested that the annual average soil emission estimate for the Salton Sea air basin was 11.4 ± 4 tons day⁻¹, representing ~ 30% of the extant NO_x inventory and 10 times larger than the air basin's inventory value for soil emissions (Lieb et al., 2024). The Almarez et al. (2018) estimates would increase the statewide NO_x budget by 20 to 51% compared to CARB's emission inventory. These estimates are not based on annual soil NO_x emission measurements, which limits the study results. In addition to the review on soil NO_x emissions, this review also covers ammonia (NH₃) and nitrous oxide (N₂O) soil emissions. Soil NO_x and N₂O emissions are produced through the microbial processes of nitrification and denitrification and can occur as a result of or separately from soil management practices such as irrigation and fertilization. Ammonia emissions from agricultural soils are dominantly derived from manure application, synthetic N fertilizers, liming, and irrigation practices. It is therefore important to understand the management and environmental conditions affecting the production and emissions of all three trace gases. The dearth in annual emission observations require a further review of the available scientific literature, pertinent databases, and emission estimation methodologies that is presented in this report.

2. Background

Soil emissions of NO_x , N_2O , and NH_3 significantly influence atmospheric chemistry and contribute to air pollution, N deposition, and greenhouse gas emission. This literature review explores the global context of these soil-derived emissions, both historically and in the present day, with a particular focus on California, where agricultural practices, combustion engines, industry, and climate conditions influence and inform regulatory frameworks to mitigate the negative effects of these pollutants.

Historically, major emission increases of soil NO_x, N₂O, and NH₃ have been linked to agricultural expansion, intensification, and synthetic N fertilizer use. Before the mid-20th century, natural processes such as biological N fixation and wildfires were the primary sources of soil N trace gas emissions. However, with the Green Revolution (1950s–1970s), synthetic N fertilizer use increased dramatically, significantly elevating NO_x, N₂O, and NH₃ emissions (Galloway *et al.*, 2008). Research indicates that global NH₃ emissions from agricultural soils increased by 20–30% between 1900 and 2000 due to intensified farming practices (Erisman *et al.*, 2008; Erisman *et al.*, 2013). Simultaneously, NO_x and N₂O emissions increased as N-based fertilizers promoted microbial nitrification and denitrification processes (Davidson, 1991).

In California, agricultural expansion in the early 20th century marked a turning point for soil N emissions. The Central Valley became a major contributor due to its intensive crop production practices and synthetic fertilizer use (Tomich *et al.*, 2016). Historical records show that NO_x , N_2O , and NH_3 emissions in the state were relatively low before industrialized agriculture. However, by the 1960s, widespread fertilizer application led to increased soil-derived N trace gas emissions (Matson *et al.*, 1997).

Currently, soil NO_x emissions account for approximately 20–30% of total atmospheric NO_x globally (Table 1), with hotspots in agricultural regions such as the U.S. Midwest, China, and India, and in Africa's Sahel region (Steinkamp and Lawrence, 2011; Aneja *et al.*, 2012). Soil NH₃ emissions have also increased globally due to rising livestock production and manure management (Behera *et al.*, 2013). Climate change may exacerbate these emissions in some regions through increased temperature and precipitation changes, altering and accelerating soil microbial activity (Butterbach-Bahl *et al.*, 2013).

Model	World	With CRF	Soil NO _x /total NO _x	EF (FIE)	CA	Year	Ref.	Notes
	Tg N yr ⁻¹	Tg N yr ⁻¹	(%)	(%)	Gg N month ⁻¹	modeled		
	21 ±10	13					Davidson & Kingerlee 1997	based on literature
	12		21				Schlesinger & Bernhardt 2020	
	23.6					2000	Wang et al. 2017	Isotope model
Y&L	10.2	5.5±2.2	15-20¶	2.5		1995	Yienger & Levy 1995	Semi-mechanistic; empirical
Y&L + GOME	$8.9\pm\!\!8.0$	$8.9 \pm \! 8.0$	22	2.5		2000	Jaegle et al. 2005	Bottom-up & top-down combined
BDNSP + OMI	12.9 ± 3.9	$12.9\pm\!\!3.9$				2005	Vinken et al. 2014	Bottom-up & top-down combined
CASA	9.7 (1.5 kg N/ha)	9.7		2.0^{+}			Potter et al. 1996	Mechanistic. [†] EF applies to N mineralized only
IMAGE			41	15	13.4	2016	Almaraz et al. 2018	Semi-mechanistic.19.8 kg N/ha yr in CA cropland
BDSNP	10.7	9.0	20-33¶	1.5	14.35	2006	Hudman et al. 2012	Semi-mechanistic/empirical
BDISNP			40	2.5	13.4 [§]	2018	Sha et al. 2021	Semi-mechanistic/empirical. [§] Estimated for July.
CMAQv.5.1			10-13¶	0.28		2011	Rasool et al. 2019	Semi-mechanistic; process-based
DNDC			1.1	0.39	0.12-0.46	2013	Guo et al. 2020	Mechanistic; process-based
	1.8* (0.36-7.3)			0.55			Stehfest & Bouwman 2006	Statistical. *Fertilized cropland
YL95EMAC	3.13*			1.0 (±2.1)		2010	Steinkamp & Lawrence 2011	Statistical.*Fertilized cropland
NO-STAT	0.67*		5.6	0.45		2012	Aneja et al. 2021	Statistical. *Fertilized Cropland
NEI			7.7		0.925	2020		Inventory
CEPAM			2.2		0.22	2020		Inventory

Table 1. Global and California soil NO_x emission estimates based on literature reviews and modeling, and in inventories.

Abbreviations: CRF Canopy reduction factor; EF (FIE) Emission Factor (Fertilizer Induced Emissions); CA California; Y&L Yienger & Levy 1995; CONUS Contiguous United States; GOME Global Ozone Monitoring Experiment; CASA Carnegie-Ames-Stanford Biosphere; IMAGE Integrated Model for the Assessment of Global Environment; BDSNP Berkeley Dalhousie Nitric Oxide parameterization; BDISNP Berkeley Dalhousie Iowa Nitric Oxide Parameterization; CMAQ Community Multiscale Air Quality; DNDC DeNitrification-DeComposition; NEI National Emissions Inventory (U.S. EPA); YL95EMAC modified Y&L model; CEPAM California Emissions Projection Analysis Model. [¶]For CONUS for May-July 2011 according to Rasool et al. (2019).

3. Soil nitrogenous emissions and driving variables

Reactive N compounds in the atmosphere are defined as N compounds that are chemically reactive, biologically active, or radiatively active by absorbing infrared radiation or other radiation (EPA-SAB, 2011). These compounds contrast with dinitrogen gas (N₂), which is non-reactive. The reactive N forms encompass three main categories: oxidized inorganic compounds (like NO_x, HNO₃, nitrate/ nitrogen trioxide radical, and N₂O), reduced inorganic compounds (NH₃ and ammonium), and organic N variants (including urea and proteins). Reactive N forms significantly impact our environment and economy. Sutton et al. (2011a) have estimated that the European Union alone faces annual costs between \$77-354 billion from reactive N compounds' effects on health and environmental systems. Moreover, Aneja et al., (2009), the U.S. EPA-SAB (2011), Erisman et al., (2013), Battye et al. (2017), Abrol et al. (2017), and Houlton et al. (2019) describe reactive N loss to the environment as one of the major environmental challenges of the 21st century impacting climate change, energy and food security, air, water and soil quality, and human health. Experts identify reactive N as one of the 21st century's primary environmental challenges, largely because most reactive N species remain poorly regulated (Driscoll *et al.*, 2024).

3.1 NO_x emissions

NO_x compounds, particularly NO and NO₂, play a central role in various atmospheric processes. These compounds orchestrate complex chemical reactions leading to smog formation, ozone production, and acid rain development (Warneck, 1999). In urban areas, high NO concentrations catalyze reactions with methane, carbon monoxide, and volatile organic compounds (VOCs), while rural environments see significant ozone production through NO's interaction with natural VOCs (Trainer *et al.*, 1993; Aneja *et al.*, 1996; Aneja *et al.*, 2008a, 2009; Romer *et al.*, 2018; Aneja *et al.*, 2021; Geddes *et al.*, 2022).

Nitric oxide (NO) is a highly reactive compound. When NO enters the atmosphere, it reacts with hydroperoxyl radicals (HO₂) to form NO₂ and hydroxyl radicals (1) (Williams *et al.*, 1992b). Both NO and NO₂ are free radicals. Nitric oxide (NO) reacts with ozone (O₃) to form N dioxide (NO₂) (2), and under the influence of sunlight, NO₂ photodissociates to reform O₃ (3,4) (Williams *et al.*, 1992b). NO_x represents the sum of NO and NO₂.

$$NO + HO_2 \rightarrow NO_2 + OH$$
 (1)

$$NO + O_3 \longrightarrow NO_2 + O_2$$
 (2)

$$NO_2 + hv \rightarrow O + NO$$
 (3)

$$O + O_2 + M \longrightarrow O_3 + M \tag{4}$$

When NO_x compounds combine with atmospheric moisture, they form nitric acid (HNO₃), contributing to acid rain and fine particulate matter (PM_{2.5}) formation. The oxidation of NO₂ may result in HNO₃ and nitrate, or with NH₃, the formation of ammonium nitrate, all of which are

components of N deposition and redistribution (Williams *et al.*, 1992b). Ammonium nitrate is the most common compound of PM_{2.5} in the San Joaquin Valley. These pollutants pose serious health risks, particularly respiratory issues and cardiovascular complications, leading to the establishment of strict regulatory standards by the USEPA (Lelieveld *et al.*, 2015).

NO_x enters our atmosphere through both natural and human-made pathways (Aneja *et al.*, 1995; Aneja *et al.*, 1996; Aneja *et al.*, 2008a, 2009; Bray *et al.*, 2019; Houlton *et al.*, 2019; Schlesinger and Bernhardt, 2020). While lightning strikes and soil microbes represent natural sources, fossil fuel combustion dominates global NO_x production, accounting for over 50% of emissions. Soils contribute significantly to the global NO_x budget (Table 1). Published field measurements and inventories show substantial NO emissions from tropical savannas (Poth *et al.*, 1995), successional pastures (Keller and Reiners, 1994), and intensively managed agriculture (Valente and Thornton, 1993; Aneja *et al.*, 1996; Aneja *et al.*, 1998; Driscoll et al., 2024).

Some sources of NO_x emissions have dual drivers, such as wildfire emissions influenced by land management practices and soil NO emissions (Bray *et al.*, 2019; Bray *et al.*, 2021). Research indicates that soil NO_x is primarily emitted as NO, which emission rates vary widely based on meteorological conditions, physicochemical soil properties (pH, soil moisture content), and N inputs from deposition, fertilizer, or manure application (Sullivan *et al.*, 1996; Schlesinger and Bernhardt, 2020). Despite the significant contribution of these emissions to atmospheric NO_x budgets, current regulation focuses on industrial and combustion sources while agricultural emissions remain largely uncontrolled (EPA-SAB, 2011).

Nitric oxide is produced through both biotic (microbial) and abiotic (chemical) pathways. Microbially, NO is generated via nitrification, the aerobic transformation of ammonium to nitrite via hydroxylamine and then to nitrate (5), and denitrification, the anaerobic reduction of nitrate to N gases. Abiotic reactions can also contribute, especially in the presence of certain soil conditions. In a low pH environment (pH <5), NO forms by abiotic chemical decomposition of the protonated form of nitrite (NO₂⁻), nitrous acid (HNO₂), via oxidation of organic or inorganic components of the soil (Van Cleemput and Baert, 1984; Van Cleemput and Samater, 1996; Venterea and Rolston, 2000b). Nitric oxide may also form as an intermediate when NH₂OH is oxidized to NO₂⁻ (Hooper and Terry, 1979). The effect of pH on NO emissions is variable. While higher pH enhances nitrification, and thus, potentially, NO formation, a low soil pH may enhance NO production due to the above-mentioned reactions involving NO₂⁻ \Leftrightarrow HNO₂.

Most of the NO emitted from soils is a by-product of nitrification (Davidson, 1991). Therefore, the factors that increase nitrification rates are the factors that potentially increase NO emissions, the most important and often rate-limiting variable being the availability of ammonium. Soil moisture must be sufficient for microbial nitrification to occur, but at higher soil water contents,

NO is typically consumed and converted to N₂O or dinitrogen before it is emitted from the soil.

The water-filled pore space (WFPS, ratio of volumetric soil water content to total soil porosity) has been used to predict the ratio of NO to N₂O emitted from the soil if adequate substrate for nitrification or denitrification is available (Potter et al., 1996). In laboratory studies, NO exceeded N₂O emissions rates at WFPS <60%, and at WFPS >60%, N₂O emissions dominated the emissions (Davidson, 1992b). The WFPS 60% has empirically been found to be the threshold when aeration is beginning to limit microbial processes in many soils (Linn and Doran, 1984; Potter et al., 1996). Often, N₂O emissions start rising at WFPS >60% (Williams et al., 1992b; Hall et al., 1996; Bateman and Baggs, 2005). When soils are wetted after prolonged dry periods, very large but short-lived pulses of NO emissions have been observed, especially with the first wet-up after a prolonged dry period (Davidson et al., 1991a; Davidson, 1992b, a, 1993; Valente and Thornton, 1993; Hall et al., 1996; Eberwein et al., 2020). Ammonium accumulates in dry soil because nitrification is more sensitive to low soil moisture than ammonification (Hartley and Schlesinger, 2000). The NO is initially produced abiotically. The initial phase may occur quickly (< 1 hour) and is subsequently followed by the biological processes of ammonia oxidation and nitrite oxidation (Davidson, 1992b, a; Slessarev et al., 2021). The second phase of microbial NO production after rewetting dry soil lasted about 36 hours in four different California soils (Slessarev et al., 2021). Pulsing has been observed in a seasonally dry forest, with NO fluxes increasing by two orders of magnitude within 2-6 hours (Davidson et al., 1991b) and in the desert south of Los Angeles (Sha et al., 2021; Eberwein et al., 2020). Algorithms describing pulsed NO emission have been included in models (Steinkamp and Lawrence, 2011; Hudman et al., 2012; Rasool et al., 2019). Substantial pulses of NO may occur in California's agricultural soil in the fall with the first rainfall, and the magnitude of such pulses likely depends on the accumulated substrate near the soil surface and the degree of soil moisture occurring with rewetting (Davidson, 1992b). A similar effect of rewetting has been documented for NH₃ emissions (Krichels et al., 2023).

Whether NO is consumed or emitted also depends on the location of the ammonium being nitrified. The majority of soil NO_x emissions originate in the top few cm's of soil (Peirce and Aneja, 2000). If nitrification takes place near the soil surface, e.g., as a result of surface application of N fertilizer or manure, NO may be emitted even when the bulk soil water content is high (Matson *et al.*, 1996). For example, studies comparing NO_x emissions after surface and subsurface fertilization have shown that fluxes from surface-fertilized plots were up to an order of magnitude higher than those from subsurface-fertilized plots (Matson *et al.*, 1996). Similarly, NO emissions were several-fold higher after broadcast urea than after injecting anhydrous ammonia in a Minnesota corn field (Venterea *et al.*, 2005). Horwath & Burger (2013) measured very high NO fluxes after flood irrigation of a field with ammonium-containing lagoon water. One explanation for this observation is that the application of fertilizer lower in the soil profile increases the diffusion path length to the surface where the emission occurs and provides opportunities for NO reduction (Hall *et al.*, 2018).

Soil temperature near the surface (1 to 5 cm depth) is another key variable affecting the magnitude of NO efflux. It affects microbial activity, production of NO, and transport of gases, as well as the solubility of ammoniacal substrate. Increasing soil temperatures increase NO production and efflux. At temperatures above 15°C, the relationship between NO_x emissions and temperature may be exponential until a maximum is reached at around 30° - 35°C due to inhibition of growth of autotrophic nitrifiers at temperatures above 40°C (Focht & Verstraete 1977; Williams et al. 1992). Heterotrophic nitrifiers, generally fungi, which may occur in high-temperature environments, have higher heat tolerance (Stroo et al. 1986), but heterotrophic nitrification is mainly known as

potential source of N₂O than NO. NO_x emissions that increased at temperatures >35° have been reported from field experiments in Imperial Valley (Oikawa et al. 2015). The relationships between temperature and NO_x emissions were investigated by Wang et al. (2023) who fit exponential functions to the relationship between NO₂ column densities and air temperature in non-urban land in California and found peak NO₂ column amounts in croplands and scrublands on average at about 30°C, followed by a plateau of NO₂ concentrations at higher temperatures. In forests and barren land, the highest NO₂ amounts were observed at 33-34°C, and at higher temperatures, the column NO₂ did not increase anymore. To improve estimates of measured NO_x fluxes, Matson et al. (1997) calculated curves of diel (day & night) NO_x flux based on measurements and developed a method to derive normalized diel curves from mid-day measured fluxes. Although soil temperature influences microbial, physical, and chemical processes to varying degrees, variables such as ammonium availability near the soil surface, soil moisture, soil tortuosity, soil pH, and others also regulate NO_x emissions, and any of these factors may control the magnitude of the emissions, depending on the circumstances. For example, Venterea & Rolston (2000a) measured extremely high NO fluxes – between 100 and 1000 ng NO-N cm⁻² h⁻¹ (corresponding to 10-100 g NO-N ha⁻ 1 h⁻¹) – for four weeks in a tomato field in Yolo County near locations in the field where anhydrous ammonia had been injected to depth of 15 cm. The flux measurements were not representative for the entire field, but data such as these illustrate how specific processes, in this case the sustained microbial production of NO2⁻ and abiotic decomposition of HNO2 yielding NO, can drive emissions. Conversely, warm soil conditions do not lead to NOx emissions if substrate for nitrification is not available or if the soil is too dry for nitrification to occur. Temperature alone does not control NO_x flux and by itself may not reliably predict the magnitude of NO_x emissions. Figure 1 shows the effect of temperature on NO_x emission in a furrow-irrigated corn cropping system.



Figure 1. NO_x flux in relation to soil temperature at 5 cm during the course of one day at three locations within a corn field in Yolo County (Burger and Horwath 2013). The fluxes represented by the red and black symbols were measured at the edge of a corn field (WFPS 43%) and those represented by the blue symbols were measured within the corn field (WFPS 46%).

Nitric oxide has low solubility (0.0056 g/100 mL at 20°C), but NO₂ hydrolyzes. The plant canopy may absorb NO₂ through stomates if the NO₂ concentration in the atmosphere is greater than 50 ppb (Hanson and Lindberg, 1991).

Nitric oxide is also an obligate intermediate compound produced during denitrification, the transformation of nitrate (NO_3^-) or nitrite (NO_2^-) to dinitrogen (N_2) by soil microorganisms using nitrate or nitrite as electron acceptors in respiration (6).

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$$
 (6)

Reports of significant quantities of NO produced from the soil in the denitrification pathway (2) and emitted to the atmosphere are rare (e.g., Remde *et al.* 1993; Krichels et al. 2022). Denitrification, which is inhibited by oxygen (O₂), generally occurs when soil water content is high and/or the oxidation of reduced carbon (C) compounds have depleted O₂. Anaerobic conditions allow reactions that further reduce NO while gaseous transport in the soil is impeded under such conditions (Williams *et al.*, 1992b).

HONO, the gaseous form of nitrous acid (HNO₂), is a source of hydroxyl radicals (OH) and NO in the atmosphere (Su et al., 2011), where NO is produced by photolysis of HONO on a time scale of about 30 minutes (Oswald et al., 2013). Donaldson et al. (2014) showed how surface acidity, not only soil solution pH, also controls the release of HONO from soil. Studies in the laboratory and field experiments have shown that HONO is released from soil, both abiotically from NO2⁻ on acidified surfaces in soil (and aerosols) and directly by ammonia-oxidizing bacteria (Su et al., 2011; Oswald et al., 2013; Donaldson et al., 2014; Liu et al., 2019; Tang et al., 2019). Low soil pH favors both abiotic NO production and HONO release (Van Cleemput and Samater, 1996; Venterea and Rolston, 2000b; Su et al., 2011). Oswald et al. (2013) demonstrated in laboratory experiments with various soils that ammonia-oxidizing bacteria directly release HONO and NO in about equal quantities, even in pH-neutral and alkaline soils, and this suggests ammoniacal fertilizers as drivers of both HONO and NO. Hydroxylamine (NH₂OH), an intermediate product of ammonia oxidation, may also be a source of NO, N₂O (Hooper and Terry, 1979), and HONO (Ermel et al., 2018). Soil moisture is another factor that significantly influences HONO emissions. In laboratory experiments, the highest rate of HONO emissions occurred at a WFPS of 17% (Cheng et al., 2025).

At an agricultural site in the North China Plain, HONO soil emissions were enhanced by a factor of three after ammonia-based fertilizer application (180 kg N ha⁻¹), with peak emission rates of 2.9 g HONO-N h⁻¹ ha⁻¹ (Xue *et al.*, 2021). Tang et al. (2019) similarly identified soil as an important HONO source in the North China Plain.

Modeling and field measurements have shown that NO_2^- , an intermediate compound in nitrification, can be a source of HONO (Liu *et al.*, 2019). Other sources are redox reactions of NO_2 in the atmosphere and adsorbed nitric acid (HNO₃) or particulate nitrate under irradiated conditions (Liu *et al.*, 2019). Ground surfaces and particulate NO_2^- can also be a sink for HONO at night, acting like a reservoir for HONO emission the following day and accounting for 30% of the source of daytime HONO (VandenBoer *et al.*, 2014). Substantial pulses of HONO, in addition of NO, may also be emitted from biological soil crusts in dryland systems upon rewetting (Weber *et al.*, 2015).

HONO emissions can be measured with a long path absorption photometer (LOPAP) (Heland *et al.*, 2001), by Ambient Ion Monitor-Ion Chromatography (AIM-IC) along with other water-soluble gases and particulates (VandenBoer *et al.*, 2014), and by Incoherent Broadband Cavity Enhanced Absorption Spectroscopy (IBBCEAS) with dynamic chambers positioned some distance (< 1m) above the soil surface (Tang *et al.*, 2019). In 2010, a Relaxed Eddy Accumulation (REA) system, which determines HONO vertical mass flux based on upward and downward drafts and HONO concentrations within the drafts, measured upward HONO flux at the Kern County Cooperative Extension site in Bakersfield during daytime (Ren *et al.*, 2011; VandenBoer *et al.*, 2014). The same REA system was used at Blodgett Forest, California, in July 2009, where HONO fluxes were small in comparison to those measured in Bakersfield (1.27 ppb HONO h⁻¹), most likely due to the low levels of reactive N at the forest site (Ren *et al.*, 2011).

In California, only a few measurements of HONO flux have been made. The evidence that HONO emissions from soil increase tropospheric NO₂ concentrations, produce hydroxyl radicals in the troposphere, and affect air quality calls for quantifying HONO emissions from California soil, including N fertilized cropland soil.

3.2 Ammonia

Ammonia (NH₃) plays a particularly crucial role in the global N cycle and represents a major anthropogenic source of reactive N. Agricultural activities, especially the use of animal manure and synthetic fertilizers, are the primary sources of NH₃ emissions. The loss of reactive N as NH₃ poses significant problems for both agricultural systems and the environment. From an economic perspective, this N loss represents substantial foregone fertility - assuming crops use N with ~33% efficiency, thus preventing NH₃ emissions could save approximately \$16 billion annually (Schlesinger and Hartley, 1992; Galloway *et al.*, 2004; Aneja *et al.*, 2009; Sutton *et al.*, 2011a; Sutton *et al.*, 2011b; Fowler *et al.*, 2015; Battye *et al.*, 2017; U.S. EPA, 2018; Houlton *et al.*, 2019).

The environmental impacts of agricultural ammonia emissions extend far beyond farmland (Bleeker *et al.*, 2009). When NH₃ reacts with acidic atmospheric compounds, it forms fine particulate matter (PM_{2.5}) (Baek *et al.*, 2004). High PM_{2.5} concentrations can cause adverse health effects, premature death, reduced visibility, and regional haze., Furthermore, when NH₃ deposits in ecosystems, it can cause degradation and increase soil N cycling rates, leading to higher N₂O emissions. The economic cost of excess reactive N emissions in the European Union alone is estimated at \$77-354 billion annually (Davidson, 2009; Bobbink *et al.*, 2010; Kwok *et al.*, 2013; Zhuang *et al.*, 2014).

Since the 1900s, synthetic N fertilizer use, and N-fixing crop cultivation have expanded dramatically. The increase in synthetic N fertilizer has led to higher global emissions of NH₃. The

Food and Agriculture Organization predicts South Asian fertilizer usage will more than double between 2006 and 2060. From 2002 to 2016, there have been substantial increases in atmospheric NH₃ emissions over several of the world's major agricultural regions (Paulot *et al.*, 2014), for example, the U.S. (2.61% yr⁻¹), the European Union (1.83% yr⁻¹), and China (2.27% yr⁻¹) (Warner *et al.*, 2017). Li et al. (2016) report an increasing proportional deposition of ammonium from the atmosphere over the United States, reflecting the increasing emissions of NH₃. Similar trends are seen in China (Zhan *et al.*, 2015).

Ammonium in soils is mineralized from soil organic matter and from organic inputs, such as plant residues, animal manure, sewage sludge, and organic fertilizers in dry or liquid forms, as well as from synthetic fertilizers applied as solutions, salts, or as anhydrous ammonia. Soil ammonium is either taken up by plants and microbes, nitrified (ammonia oxidation), leached, or volatilized as ammonia.

Ammonia volatilization is strongly influenced by soil moisture, with dry conditions often exacerbating emissions due to the accumulation of ammonium in surface soils (Sutton *et al.*, 2009). Low soil moisture reduces plants and microbial assimilation of ammonium, leading to increased NH₃ losses, particularly in sandy soils and alkaline environments (Sommer and Ersbøll, 1996). Furthermore, fertilization of dry soils can result in higher NH₃ emissions due to slower N incorporation into the soil matrix (Rochette *et al.*, 2013). Incorporating irrigation scheduling and urease inhibitors can help mitigate NH₃ volatilization under dry conditions (Misselbrook *et al.*, 2004).

Ammonia volatilization occurs when the ammonium source is at or near the soil surface, for example, in the form of broadcast synthetic fertilizer pellets, but ammonium near the soil surface may also result from applying solutions containing ammonium to the soil surface. Furthermore, as soils dry, the concentration of ammonium in the soil solution increases, hence the concentration of NH₃ and the potential for volatilization of NH₃. High soil pH increases ammonia volatilization compared to lower soil pH. Soil and air temperature also affect NH₃ volatilization with increasing temperature increasing the volatilization. Higher soil surface temperatures increase the loss of NH₃ from soil and enable more rapid conversion from NH₃ aqueous to NH₃ air.

Precipitation or water applications may transport ammonium deeper into the soil, which reduces volatilization, as does the incorporation or deep placement of ammoniacal materials in the soil (Nelson, 1982). Generally, moist soils emit less NH₃ than drier soil due to the lower gas diffusivity in wetter soil, however, moist soils can emit higher amounts of applied fertilizer NH₃ than drier soils when soil moisture enhances the rate of urea hydrolysis (Potter *et al.*, 2003).

Livestock manure amendments and organic and inorganic fertilization are the largest sources of NH₃ emissions from soils (Anderson *et al.*, 2003). Sources of NH₃ volatilization other than soils are biomass burning (enhanced inorganic N), industrial processes, automobiles, and oceans. Ammonia volatilization from soils is highly sensitive to both pH and N application rates, with less acidic conditions and greater ammonium concentrations generally driving the largest fluxes (Duan and Xiao, 2000). The use of nitrification inhibitors can increase NH₃ emissions. Most N inhibitors are designed to slow or eliminate nitrification without impacting N mineralization and ammonification. Inhibition of nitrification can lead to an accumulation of ammonium in soils, especially in fertilized agroecosystems, if plants and microbes are unable to rapidly immobilize increased N. This can subsequently increase rates of NH₃ volatilization (Kim *et al.*, 2012; Cui *et al.*, 2021). Ammonia volatilization is generally favored at neutral to alkaline pH, although Cui et

al. (2024) reported a 31% increase in NH₃ emissions in acid soils treated with a chemical nitrification inhibitor. Nitrification and nitrate leaching tend to acidify soils (Tian and Niu, 2015), and thus, nitrification inhibition could result in pH conditions that favor NH₃ emissions.

3.2.1. Regional and global NH₃ emissions

The Central Valley, with its large-scale crop and dairy production, is responsible for a significant portion of the state's agricultural ammonia emissions. Ammonia emissions are notably high in regions with concentrated livestock operations, such as the San Joaquin Valley (Vechi *et al.*, 2023). According to the *California Dairy and Livestock Database* (CADD), the state-wide dairy cow herd has been declining since 2013 at the rate of -1.3% p.a. with a projected decrease of 22% between 2013 and 2030. Atmospheric N deposition can also drive soil NH₃ emissions, with emission rates increasing with high soil pH found in many soils in the region (Krichels *et al.*, 2023). Krauter et al. (2002) estimated an NH₃ emissions factor of 3.2% of fertilizer application for California's Central Valley. More details on California emissions are found in Section 4.

Ammonia volatilization is likely to exhibit high temporal variability due to the dynamic nature of the associated drivers (e.g., pH, ammonium, moisture). Therefore, continuous measurements are required to accurately measure NH₃ emissions. However, few studies have measured continuous fluxes due to additional challenges to quantifying NH₃ emissions from soils. Ammonia is a "sticky" gas, and thus, tubing and instrumentation must be lined with materials such as Teflon to avoid gas loss during collection and analysis. Ammonia is also easily solubilized in water. Condensation in incubation vessels, tubing, and instruments can remove NH₃ from the gas phase leading to underestimates of emissions (Scotto di Perta *et al.*, 2020). Soil emissions have been estimated with passive collectors, open dynamic chambers, and dynamic closed chambers using direct laser absorption spectroscopy and cavity ring-down spectroscopy (CRDS). Data from dynamic closed soil surface flux chambers compared well with micrometeorological data for NH₃ emissions and provided the added benefit of facilitating replicate treatment comparisons (Scotto di Perta *et al.*, 2020). Chamber-based measurements can also be more directly coupled with data on soil, plant, and microbial drivers at small spatial scales.

Based on observational emissions data, Aneja et al. (2020) generated a global map for NH₃ emissions (NH₃_STAT) in kg NH₃-N yr¹ per grid cell (Figure 2a). Figure 2b is the spatial distribution of global NH₃ emission from agricultural soil based on Emissions Database for Global Atmospheric Research (EDGAR). Figure 3 provides an overview of the soil emissions from the Continental United States (CONUS). The NH₃_STAT is an observational emissions data model while EDGAR is an emission factor-based approach. Table 2 summarizes the global and regional NH₃ emissions (in Tg N yr⁻¹) from agricultural soils from different emission inventories. Sources of NH₃ volatilization other than soils are biomass burning (enhanced inorganic N), industrial processes, automobiles, and oceans (Schlesinger and Bernhardt, 2020).



Figure 2. Comparison between the global emission results from (a) NH_3 _STAT, (b) EDGAR, and (c) absolute difference between the two models (in tons of N yr⁻¹ per grid cell⁻¹). (Source: Aneja et al., 2020)



Figure 3. Comparison between the US results from (a) NH_3 _STAT, (b) EDGAR, and (c) absolute difference between the two models (in tons N yr⁻¹ per grid cell). (Source: Aneja *et al.*, 2020)

Inventory	Year	Global			Continental United States			India			China		
		Mineral fertilizer	Manure	Total	Mineral fertilizer	Manure	Total	Mineral fertilizer	Manure	Total	Mineral fertilizer	Manure	Total
NH ₃ _STAT	2012	5.9	8.0	13.9	0.8	1.0	1.8	0.6	0.9	1.5	0.7	1.0	1.7
MASAGE	2008	9.4	24.0	33.4	0.5	1.7	2.2				3.0	4.8	7.8
MIX	2010									6.1			7.4
Beusen	2000	10–12	16–27	27–38		2.1	2.1						
et al. (<u>2008</u>)													
EDGAR v4.2	2008	24.0	8.6	32.6	1.6	1.0	2.6				6.8	1.9	8.7
Goebes et al. (<u>2003</u>)	1995				0.7								
U.S. EPA (<u>2006</u>)	2002					1.7							
Huang	2006										2.6	4.4	7.0
et al. (<u>2012</u>)													
Streets	2000										5.5	4.1	9.6
et al. (<u>2003</u>)													

Table 2. Global and Regional NH_3 Emissions (in Tg N yr⁻¹) from Agricultural Soils Summarized from Different Emission Inventories. (Source: Aneja et al., 2020)

3.3 Nitrous oxide

Greenhouse gas emissions to the atmosphere since the late 20th century represent humanity's largest influence on climate. While carbon dioxide (CO₂) is the primary greenhouse gas, N₂O is also critically important, with a global warming potential (GWP) approximately 300 times that of CO₂ over a 100-year period (Myhre *et al.*, 2013). Beyond its warming effects, N₂O contributes to stratospheric ozone depletion and persists in the atmosphere for about 114 years, indicating its long-lasting global impact (Forster *et al.*, 2007; Ravishankara *et al.*, 2009).

Atmospheric N₂O concentrations have been monitored at Mauna Loa, Hawaii, since 1978, with earlier levels determined from Antarctic ice cores. Concentrations remained relatively stable until the Industrial Revolution (Flückiger *et al.*, 2002), after which they increased by 18% from approximately 270 ppb to the current level of 331 ppb. This significant rise primarily stems from increased human activities, particularly agricultural practices (Aneja *et al.*, 2019).

For the period 2006-2011, annual global N₂O emissions totaled 17.9 Tg N yr⁻¹ (Ciais *et al.*, 2014). Natural sources, including land and oceans, account for 11.0 Tg N yr⁻¹, while agricultural activities represent the primary anthropogenic source at 5.6 Tg N yr⁻¹ (Schlesinger and Bernhardt, 2020). Since 1990, soil N₂O emissions have increased from 3.5 to 4.1 Tg N yr⁻¹, driven by growing food, fiber, and energy production, along with climate change and agricultural intensification (IPCC, 2006). Between 1961 and 2010, global N₂O emissions from manure usage grew from 1.17 to 2.03 Tg N yr⁻¹ (1.1% annual increase) (Smith and Massheder, 2014), while emissions from synthetic fertilizers rose more dramatically from 0.14 to 1.40 Tg N yr⁻¹ (3.9% annual increase). Synthetic fertilizer emissions are projected to surpass manure-related emissions within a decade (Tubiello *et al.*, 2013). Other sources, including fossil fuel combustion, industrial processes, and biomass burning, contribute relatively minor amounts to total N₂O emissions.

Significant uncertainties remain in the global N₂O budget, particularly regarding agricultural soil emissions (Oertel *et al.*, 2016). Limited understanding of N₂O emission mechanisms may have led to underestimating agriculture's role in rising atmospheric N₂O levels. As food and energy production increase alongside climate change and agricultural intensification, soil and groundwater N₂O emissions are expected to rise, necessitating an updated global N₂O budget. Intensive fertilizer use has increased emissions of reactive N compounds, including N₂O, through soil nitrification and denitrification processes.

The ratios of N₂O to nitrate (nitrification) and N₂O to dinitrogen (N₂ primarily via denitrification) products are crucial parameters in the global budget, influenced by various interacting physical, chemical, and biological factors. Key variables affecting N₂O emissions include soil moisture, aeration, temperature, available C, N content, pH, and salinity. N₂O emissions increase during nitrification under conditions of low oxygen, high soil moisture, low ammonium concentrations, non-neutral pH, and higher temperatures (Granli and Bøckman, 1994). During denitrification, N₂O production increases with high nitrate levels, high C availability, low pH, high temperature, low N₂O reductase activity, and 60-90% water-filled pore space (Stehfest and Bouwman, 2006; Rashti *et al.*, 2015; Wang *et al.*, 2017). High soil moisture levels promote anaerobic conditions that favor

denitrification, although fully saturated soils may reduce N₂O to N₂ before it is emitted into the atmosphere, though direct evidence is limited (e.g., Burger et al. 2008) by the difficulty in measuring N₂ fluxes from soils (Almaraz *et al.*, 2020). The percentage of water-filled pore space (WFPS) and direct soil O₂ measurements are the best variables to predict soil moisture effects and redox conditions on the production, consumption, transport, and efflux of N₂O (Anthony and Silver, 2024). Low oxygen levels may also occur when high microbial O₂ demand in soils rich in organic C or when high root O₂ demand exceeds the rate of oxygen diffused through the soil (Silver *et al.*, 1999). In such conditions, the resulting anaerobic environments can shift microbial processes toward denitrification and increase the production of N₂O. Temperature affects microbial activity, generally accelerating both nitrification and denitrification processes at higher temperatures, thus leading to increased N₂O emissions. Additionally, soil pH can regulate the activity of nitrifiers and denitrification pathways and increasing the N₂O: N₂ ratio during denitrification.

In agricultural soils, N₂O emissions are driven by a combination of biological, abiotic, and environmental factors, all of which interact with agricultural management practices. The primary biological processes responsible for N₂O production include nitrification and denitrification, which are mediated by diverse microbial communities (Robertson and Tiedje, 1987; Firestone and Davidson, 1989; Wrage *et al.*, 2001; Stein, 2011). Other microbial pathways, such as heterotrophic nitrification, fungal denitrification, dissimilatory nitrate reduction to ammonium (DNRA), anaerobic ammonium oxidation (Anammox), and complete ammonia oxidation (Comammox), and iron-coupled ammonium oxidation (Feanmox) also contribute to N₂O production, though their significance varies based on soil type, pH, redox, and moisture conditions (Anderson *et al.*, 1993; Stevens *et al.*, 1998; Silver *et al.*, 2001; Clément *et al.*, 2005; Yang *et al.*, 2012).

In addition to biological processes, abiotic factors play a significant role in N₂O emissions. Reactions involving hydroxylamine and soil minerals like manganese and iron oxides can lead to the abiotic production of N₂O through the chemical decomposition of N intermediates (Mann and Quastel, 1946; Bremner and Shaw, 1958; Nelson and Bremner, 1970). This process, referred to as hydroxylamine decomposition, is influenced by the availability of these redox-active metals in soils. Another abiotic process, chemodenitrification, involves the chemical reduction of nitrate or nitrite in the presence of Fe (II) and organic matter under anoxic conditions, further contributing to N₂O emissions. These abiotic pathways are more likely to occur in soils with low O₂ availability, such as waterlogged or flooded soils, or during high rainfall or irrigation events where microbial activity shifts towards denitrification and other reductive processes (Stevenson and Swaby, 1964; Stevenson *et al.*, 1970; Van Cleemput, 1998).

3.3.1. Regional and global N₂O emissions: California vs. other regions

Aneja et al. (2019) developed a global and a Continental US (CONUS) emission inventory for N_2O from agricultural soils (Figure 4) and a using emissions observation for N_2O . A summary of N_2O emissions from different inventories is also provided in Table 3.



Figure 4. Comparison between the global results from (a) N_2O_STAT , (b) EDGAR, and (c) absolute difference between the two models (in ton N_2O yr⁻¹ per grid cell). The maps are generated using ILWIS v3.8.5 (https://52north.org/ software/software-projects/ilwis/ilwis-3/). (Source: Aneja *et al.*, 2019)



Figure 5. Comparison between the results for continental United States (CONUS) from (a) N₂O_STAT, (b) EDGAR, and (c) EPA/USGS (in ton N₂O yr⁻¹ per grid cell). The maps are generated using ILWIS v3.8.5 (<u>https://52north.org/software/software-projects/ilwis/ilwis-3/</u>). (Source: Aneja *et al.*, 2019)

Emission inventory	$N_2O (Tg N yr^{-1})$					
	Global	US	India	China		
N ₂ O_STAT	3.75	0.400	0.412	0.300		
EDGAR	4.49	0.432	0.468	0.832		
FAOSTAT	4.07	0.350	0.440	0.686		
Bouwman et al. [2002]	2.80	_	_	_		
EPA/USGS	-	0.457	_	-		
EPA Report	_	0.529	_	_		
Aneja et al. [2012]	_	-	0.344	_		
Garg et al. [2006]	_	_	0.181	_		
Sharma et al. [2011]	_	_	0.226	_		
Gao et al. [2007]	_	_	_	0.294		
Zhou et al. [2008]	_	_	_	0.414		

Table 3 Summary of N_2O emission from different inventories. (Source: Aneja et al., 2019)

In California, agricultural soils emit 6.8 MMT (million metric tons) of carbon dioxide equivalents (CO₂e) as N₂O annually, which accounts for almost 60% of the state's total N₂O emissions (Xiang *et al.*, 2013; Tomich *et al.*, 2016) and contributes 2.3% of the total agricultural N₂O emissions in the United States (IPCC, 2013; U.S.EPA, 2024). The N₂O emissions from California agriculture are primarily from cropland soils and manure management (Tomich *et al.*, 2016), largely due to the widespread use of synthetic N fertilizers and manure in crop and livestock production systems. Cropping systems such as almonds, tomatoes, and dairy forage are especially reliant on high N inputs to sustain productivity, which increases the risk of reactive N losses to the atmosphere. These losses occur through both microbial pathways—nitrification under aerobic conditions and denitrification under anaerobic or compacted soil conditions—and are influenced by California's high temperatures, intensive irrigation, and soil properties, all of which enhance microbial activity and gaseous N losses.

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. In contrast, in the U.S. Midwest, dominated by corn and soybean systems, wetter soils and seasonal rainfall promote denitrification-driven N₂O emissions, especially after large storm events (Snyder *et al.*, 2009; Francis Clar and Anex, 2020). Although both regions have high N fertilizer use, California's drier climate, frequent irrigation, the widely adopted drip irrigation technologies, and perennial crop focus result in a different seasonal and microbial emission pattern characterized by a greater role of nitrification.

Globally, California's N emission profile aligns with other high-intensity agricultural systems like those in China and India, yet it is distinct due to the prevalence of perennial crops, year-round production, and a robust policy framework. Compared to European systems, where diversified rotations, cover crops, and tighter nutrient cycling are more common, California's large-scale monocultures and specialized systems contribute to nutrient imbalances and legacy N storage (Tomich *et al.*, 2016),). In Southeast Asia, emissions are driven by anaerobic conditions in flooded rice paddies, which produce both methane and N₂O via different microbial pathways (Stehfest and Bouwman, 2006). These contrasts underscore the need for region-specific strategies that account for distinct climate, management, and cropping system characteristics.

3.4 Soil nitrogenous emission measurements

Measuring N-gas emissions from soils is challenging. Static chambers with periodic (weekly to monthly) measurements to measure soil-atmosphere emissions are likely to miss important high or low flux events that can have outsize contributions to annual emissions estimate. The drivers of NO_x, N₂O, and N₂ emissions are often highly variable in time and space, leading to locations or periods of high emissions (Butterbach-Bahl et al., 2013). These are often referred to as hot spots and hot moments (McClain et al., 2003) of fluxes. Periodic sampling with static flux chambers can easily miss hot spots and hot moment emissions of N-gases from soils (O'Connell et al., 2022). Automated chambers coupled with cavity ringdown spectroscopy, in-field gas chromatography, or photoacoustic trace gas analyzer can be used to make continuous measurements of N₂O emissions (Van der Weerden et al., 2013; Anthony and Silver, 2021). The advantage of continuous sampling is that it increases the ability to 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. Herrera et al. (2021)

calculated spatially integrated N₂O emission rates for the SJV using nocturnal and convective boundary-layer budgeting methods using data from the NASA Deriving Information on Surface Conditions from Column and Vertically Resolved Observations Relevant to Air Quality (DISCOVER-AQ) campaign in 2013. The method could identify specific mechanisms, and notably they found fluxes that were approximately 2.5 times larger than previous inventory estimates and that animal agriculture, likely manure management, and daytime fluxes dominated the signal.

4. Impacts of soil management practices on nitrogenous emissions in California

In addition to the effects of inorganic fertilizer management, other management activities can affect N gas fluxes from agricultural soils.

4.1 Irrigation and N management effects on NO_x and N₂O emissions in California cropping systems

There are no comprehensive seasonal field studies on soil NO_x emissions in California, but rather, two surveys of NO_x fluxes in multiple cropping systems in the Sacramento and San Joaquin Valleys with relatively few measurements at each site (Matson *et al.*, 1997; Burger and Horwath, 2013). The study by Matson *et al.* (1997) was informative but has somewhat limited value today, as most farmers and ranchers today use efficient micro-irrigation approaches, such as subsurface drip irrigation, where fertilizers are applied incrementally (fertigation) throughout the growing season. Moreover, the measurements in the Matson *et al.* (1997) study were conducted past the fertilizer application season in July/August. Subsurface drip irrigation contrasts with the few applications, typically starter and side dress events, used under flood furrow and other traditional field practices common before the mid-2000s. In addition, crops grown have changed with a predominance (~70%) of orchard crops in many agricultural regions (Culman *et al.*, 2014). The Burger and Horwath (2013) study included row and field crops such as dairy forage systems, alfalfa, wheat, and processing tomatoes, and the perennial crop of almonds. Table 4 shows the range of hourly NO_x fluxes across these cropping systems with furrow irrigation, subsurface drip irrigation (SDI), and N fertilizer application comparisons.

In dairy forage production systems, NO_x and N_2O fluxes were generally higher than in other cropping systems, mainly due to the use of flood irrigation and the combined application of N through manure effluents and synthetic fertilizers (Table 4) (Burger and Horwath, 2013). The increases in both NO_x and N_2O are associated with N fertilizer input events, including manure effluent and chemical fertilizer. The potential for higher NO_x emissions from flood-irrigated forage production systems fertilized with liquid manure, make dairy systems good candidates for mitigation practices such as subsurface drip irrigation.

	Average flux	<u>SE</u>	
	g NO-N ha ⁻¹ h ⁻¹		
Wheat	0.04	0.01	
Alfalfa, 5 year old stand	0.19	0.02	
1 year old stand	0.54	0.31	
Almond, tractor row	0.06	0.01	
Tree row	0.35	0.05	
Tomato, SDI winter-fallow (179 kg N ha ⁻¹)	0.07	0.01	
SDI, winter cc (179 kg N ha ⁻¹)	0.18	0.02	
FI, zero N applied	0.10	0.03	
FI, standard N rate (162 kg ha ⁻¹)	0.22	0.0815	
FI, standard N rate, cc	0.32	0.15	
FI, 300 kg N ha ⁻¹ applied	2.79	0.64	
Silage corn, Farm A, Field 1	0.75	0.04	
FI, Farm A, Field 2	0.39	0.06	
FI, Farm B, Field 1	2.03	0.28	
FI, Farm B, Field 2	1.98	0.49	
FI, Farm C	2.43	0.55	

Table 4. Summary of mean hourly NO_x fluxes in different cropping systems.

SDI = Subsurface drip-irrigation; FI = Furrow irrigation; cc = cover crop

Subsurface drip irrigation can dramatically reduce N_2O emissions from soils. In Figure 6, a comparison of flood-irrigated and subsurface drip irrigation showed a 5-times reduction in N_2O emissions in alfalfa, a common forage production crop. N_2O emissions were significantly reduced during the alfalfa growing season. A rain event in November showed little difference between irrigation treatments, likely due to soil profile wetting during the winter precipitation event. This is a common observation in California's Mediterranean climate, where the first substantial rainfall event onto dry soil elicited N mineralization, nitrification, and denitrification, leading to emissions of NO_x and N_2O (Davidson, 1992a).



Figure 6. Seasonal N_2O emissions in alfalfa under flood (blue) and subsurface drip irrigation (red) (Brynes et al. (2015)). The arrows in green represent flood irrigation events and the blue arrow indicates the first major rain event of the season. The bar graph to the right indicates the cumulative emission by irrigation treatment. Standard errors shown as line bars. n=8.

Irrigation practices affect soil moisture levels, influencing both microbial and abiotic processes that lead to N₂O emissions. Strategies that optimize irrigation and N management can thus reduce emissions by maintaining soil conditions that limit the production of N₂O. The use of subsurface drip irrigation in processing tomato systems can dramatically reduce NO_x and N₂O emissions compared to furrow-irrigation (Kallenbach *et al.* 2010, Burger& Horwath 2013) (Figure 7; Figure 8). Mean daily NO_x emissions were 0.27 (+/- 0.06) and 0.46 (+/- 0.13) g NO-N/ha h in furrow-irrigated winter-fallow and winter cover-cropped and 0.06 (+/-0.01) and 0.17 (+/- 0.02) g NO-N/ha h in subsurface drip-irrigated treatments, respectively (Burger & Horwath 2013).



Figure 7. NO_x and N_2O flux in processing tomato fertilized with winter cover crops under furrow flood irrigation. Standard errors shown as line bars. n=3. (Burger and Horwath, 2013)


Figure 8. NO_x and N_2O flux in processing tomato fertilized with winter cover crops under subsurface drip irrigation. Standard errors shown as line bars. n=3.

Under subsurface drip irrigation in processing tomatoes, both NO_x and N_2O emissions were an order of magnitude lower compared to furrow irrigation (Figure 7; Figure 8). Overall, subsurface drip consistently results in substantial reductions in both NO_x and N_2O emissions across various crops and demonstrates its effectiveness as a mitigation strategy for N trace gas emissions across all crops observed. Figure 8 shows the effect of a winter legume cover crop on increasing both NO_x and N_2O emissions in SDI processing tomatoes. The additional available N from the cover crop in the organic form may lead to these increased emissions. The additional C inputs from the cover crops can promote denitrification, for example.

In contrast to subsurface drip-irrigation which lowered NO_x and N_2O emissions in processing tomato cropping systems, flood irrigation of corn in the Sacramento-San Joaquin Delta region of California led to high N_2O fluxes (Anthony and Silver, 2021), characterized by hot moments, i.e., spikes, of emissions (Figure 9). Similar patterns have been observed in alfalfa (Figure 10) (Anthony et al., 2023) and flooded-irrigated pasture (Figure 11) (Anthony and Silver, 2024). Continuous instrumentation allowed for the documentation of rare hot moments of emissions that accounted for a significant proportion of the annual flux.



Figure 9. Nitrous oxide emissions from soils cultivated with corn in the Sacramento-San Joaquin Delta region of CA using continuous instrumentation. Hot moments of emissions are associated with the onset of flood irrigation. Values are means and standard errors. n=9 chambers. From Anthony and Silver (2021).



Figure 10. Nitrous oxide emissions from soils cultivated with alfalfa in the Sacramento-San Joaquin Delta region of CA using continuous instrumentation. Hot moments of emissions are associated with the onset of flood irrigation. Values are means and standard errors. n=9 chambers. From Anthony and Silver (2023).



Figure 11. Nitrous oxide emissions from a peatland pasture in the Sacramento-San Joaquin Delta region of CA using continuous instrumentation. Hot moments of emissions are associated with the onset of flood irrigation. Values are means and standard errors. n=9 chambers. From Anthony and Silver (2023).

In summary, irrigation practices significantly influence NO_x and N_2O emissions from soils. Flood irrigation generally results in the highest emissions, while SDI provides the most efficient N management with minimal environmental impact. Future research should focus on optimizing irrigation-fertilization interactions to enhance N retention and mitigate greenhouse gas emissions.

4.2 The role of cover cropping and crop rotation in mitigating soil NO_x, N₂O, and NH₃ emissions

Cover crops can improve soil health and provide an N source for the following crops. Cover cropping and crop rotation are widely promoted as sustainable practices to enhance soil health and mitigate N losses (Basche et al., 2014). Rotational strategies in vegetable and grain systems also demonstrate N retention benefits under irrigation-intensive farming (Bowles et al., 2020). In California, high-input agriculture and Mediterranean climate conditions create distinct N cycling challenges. Studies highlight that cover cropping in California almond orchards can reduce N_2O emissions (Smart et al., 2011). However, Winter cover crops can also increase both NO_x and N_2O emissions during the following summer crop. Cover crops impact soil N dynamics by:

- Scavenging excess N, reducing nitrate leaching, and subsequent denitrification (Drinkwater and Snapp, 2007).
- Altering microbial communities to favor complete denitrification, reducing N₂O emissions (Mitchell et al., 2013).
- Providing residue inputs that affect soil C:N ratios, which influence nitrification and denitrification pathways (Kong et al., 2007).

Studies indicate that leguminous cover crops can increase N_2O emissions due to high N inputs, whereas non-leguminous cover crops generally reduce emissions by immobilizing soil N. Addition of compost to cover crop systems could further reduce the need for synthetic fertilizers, although

this could increase N_2O emissions (Boardman *et al.* 2018). Adding compost can reduce, but not eliminate, the need for inorganic N fertilizers, however, few studies have explored the combination of cover crops and compost amendments and thus generalizations are not possible. Crop rotation influences N emissions by:

- Enhancing soil structure and microbial diversity, leading to improved N use efficiency (Drinkwater et al., 1998).
- Interrupting continuous N cycling that favors excessive NO_x and N₂O losses (Huang et al., 2004)
- Reducing synthetic fertilizer requirements, thus lowering NH₃ volatilization risks (van Groenigen et al., 2015)
- Long-term studies demonstrate that diversified rotations incorporating legumes and cereals reduce overall N losses compared to monocultures (Tiemann et al., 2015).

Despite promising results discussed above, research gaps remain in quantifying the long-term and system-wide effects of cover cropping and crop rotation on N_2O , NH_3 , and NO_x emissions. Priorities should include more continuous datasets, and more experimentation on levels of separate and combined fertilization, irrigation, and use of nitrification inhibitors to better optimize management for emissions reduction without significant yield loss. This should happen across crop types and rangeland ecosystems. Policies promoting sustainable N management should integrate incentives for adopting these practices.

4.3. Effect of Anaerobic Digestate on soil NO_x, N₂O, and NH₃ emissions

The application of dairy anaerobic digestate to agricultural soils is increasingly promoted in California as a sustainable nutrient recycling strategy. However, its impacts on NO, N_2O , and NH_3 are complex and context dependent. The technique is not new but is only recently being implemented on select dairies in California resulting in a dearth of information on the impact of this technology on N trace gas emissions.

Studies in California have shown that organic amendments, including digestates, can increase NO emissions under certain conditions, particularly in warm, moist soils with high microbial activity (Venterea *et al.*, 2015). However, data specific to digestate-derived NO emissions in California are limited, and further research is needed.

Anaerobic digestate can influence N₂O emissions depending on the form and timing of N release. Compared to raw and solid manure, digestates often contain more mineral N (e.g., ammonium), which is readily available for nitrification and denitrification, processes that produce N₂O (Sommer *et al.*, 2003). In California cropping systems, particularly under flood irrigation and warm conditions, digestate applications have been shown to increase N₂O emissions, especially when not synchronized with crop uptake (Verhoeven *et al.*, 2017). However, emissions can be mitigated through split applications and improved timing (Dong *et al.*, 2022). Despite these insights, data specific to digestate-derived N₂O emissions in California are limited, highlighting the need for further research.

Ammonia volatilization is often higher from digestates than from raw manure due to the increased pH and increased ammonium content in the effluent (Aneja *et. al.*, 2008b). In California's semi-

arid climate, surface-applied digestate can result in substantial NH₃ losses if not incorporated quickly into the soil (Misselbrook *et al.*, 2005). Incorporation methods (e.g., injection, tillage, or SDI) are effective strategies to reduce NH₃ volatilization (Woodley *et al.*, 2020). Overall, data specific to digestate-derived NH₃ emissions in California are limited, particularly under SDI, and further research is needed.

In California, the use of dairy anaerobic digestate as a soil amendment poses both opportunities and challenges for N management. While it can improve nutrient recycling and reduce N trace gas emissions compared to unmanaged manure, its application may increase emissions of NO, N₂O, and NH₃ if not carefully managed. Adoption of best management practices—such as appropriate timing, incorporation, and SDI; and engineered solutions (Aneja *et al.*, 2008c)—can help mitigate these emissions and optimize environmental benefits.

4.4 Effect of compost on soil nitrogenous emissions

Compost derived from livestock manure, yard and food waste is increasingly used in California as a soil amendment for its benefits in enhancing soil health and diverting organic waste from landfills as regulations such as SB 1383, AB 1826, and AB 341 are enacted that mandate commercial and residential organic recycling and facilitate composting those organics. Existing studies show that N₂O emissions from compost amendments are low in California's rangelands as well as rangeland in other regions (Ryals and Silver, 2013; Kutos *et al.*, 2023; Anthony *et al.*, 2024; Wong et al., 2023). Its effect on NO and NH₃ are less well documented.

In California's irrigation-intensive and warm croplands as well as in rangelands, compost has emerged as a valuable amendment that improves soil structure, organic matter content, C sequestration, and water-holding capacity—traits especially beneficial in managing drought-prone and degraded soils in agriculture (Diacono and Montemurro, 2011; Silver *et al.*, 2018; Harrison *et al.*, 2020). Beyond these soil health benefits, compost also influences N dynamics. Compared to synthetic fertilizers, compost typically releases N more slowly, which can reduce NO and N₂O emissions by lowering mineral N availability and enhancing microbial N immobilization (Ryals *et al.*, 2014; Hall *et al.*, 2018). In California almond orchards, compost-amended soils have been shown to emit less N₂O than those receiving conventional fertilization, likely due to improved soil structure and more gradual N mineralization (CalRecycle, 2015). Compost amendments may decrease N₂O emissions when inorganic N fertilizer is used (Lazcano et al., 2021; Nichols et al., 2024). However, excess compost application can still increase emissions when N inputs exceed crop demand (Venterea *et al.*, 2011).

The effects of compost on soil N₂O emissions in California are likely to be dependent on compost type, soil properties, and management practices. For example, green waste compost with a C:N ratio above 15 has been shown in incubation studies to reduce N₂O emissions from California soils with high emission potential (Zhu-Barker *et al.*, 2015). Field studies in the California tomato system found no significant effect of compost on N₂O emissions (CalRecycle, 2015), while in a Central Valley olive orchard, green waste compost significantly reduced emissions (Curtright et al., unpublished; Figure 12). Similar results were found in international studies (e.g., Dalal *et al.*, 2010 in Australia). More site-specific evaluation under California conditions are needed to determine the regional and statewide benefits of compost amendments on soil N₂O emissions. Importantly, data on compost-derived NO and NH₃ emissions in California remain limited, and

more targeted research is needed to develop regionally relevant guidance for optimizing compost use to reduce N gases while supporting long-term soil health.

NH₃ volatilization is typically higher when organic amendments are surface applied. Yard and food waste composts tend to have a higher C:N ratio and stabilized organic N, leading to lower immediate NH₃ emissions compared to raw manure (Crohn et al., 2007). Incorporation of compost into the soil further reduces NH₃ losses (Brown et al., 2008). However, emission potential varies depending on compost maturity and environmental conditions. In California agriculture, application of yard and food waste compost generally reduces N₂O and NH₃ and, most likely, NO emissions compared to conventional fertilizers and raw manure, especially when applied at agronomic rates and incorporated into the soil. However, NO dynamics remain understudied, and emission outcomes are influenced by compost composition, soil properties, and management practices. Overall, data specific to soil compost application on N trace gas emissions in California are limited, and further research is needed.



Figure 12. Nitrous oxide flux from the soil with and without compost addition. Panels represent separate sampling years. Lighter colored points received compost in both years. Points indicate compost treatment means averaged over the three fertilizer N rates. Means are shown with error bars representing one standard error (n = 12). Green dotted lines indicate fertigation events. The precipitation amount is indicated by blue bars and the right axis.

California has been a leader in mitigation innovation. The Healthy Soils Initiative and widespread adoption of precision nutrient management demonstrate the state's investment in sustainability. These programs aim to optimize fertilizer application, promote soil organic matter, and enhance nutrient use efficiency—strategies that can reduce both direct N₂O emissions and indirect N losses. However, persistent emissions in high-input regions suggest the need for continued investment in

technologies and practices that address legacy N pools, manure-derived N losses, and spatial hotspots of emission risk. Overall, California offers a compelling example of how advanced agricultural systems can sustain productivity while moving toward environmental goals, with insights that may benefit similarly intensive farming regions around the world.

4.5 Effects of atmospheric N deposition on emissions

In the 20th century, anthropogenic sources—including fertilizer application, industrial emissions, and vehicle exhaust—significantly increased reactive N (Nr) levels in the atmosphere. This enhanced N deposition in terrestrial ecosystems ultimately stimulated soil reactive N emissions, particularly N₂O and ammonia. Both direct and indirect anthropogenic N inputs have substantially intensified reactive N cycling and the subsequent production of N gases and other reactive N compounds. Over the past three decades, regional patterns have diverged: some areas (notably Western Europe) have experienced declining N deposition, while others (especially in developing countries) have seen continuing increases. These spatial and temporal variations make soil reactive N emissions difficult to quantify accurately, contributing to persistent uncertainties in Earth system emission models (Harris *et al.*, 2022; Cen *et al.*, 2024).

5. NO_x emission models

Global annual soil NO_x emissions have been estimated based on literature values from various ecosystems at 21 (\pm 10) Tg NO_x-N (Davidson and Kingerlee, 1997) (Table 1). Schlesinger & Bernhardt (2020) estimated global annual soil emissions at 12 Tg NO_x-N. Modeling yielded similar estimates. For example, Potter et al. (1996) modeled global soil NO emissions as 9.7 Tg NO_x-N, Yienger & Levy (1995) as 10.2 Tg NO_x-N, and Hudman et al. (2012) as 10.7 Tg NO_x-N. Wang et al. (2017) estimated global annual soil NO_x-N emissions of 23.6 Tg NO_x-N, for worldwide cropland 6.0 Tg NO_x-N, and for North America 0.9 Tg NO_x-N.

Some of the global emission estimates were lowered when the adsorption of NO_x onto plant canopy surfaces was considered and included in the models, although we are not aware of any field studies of plant canopy NO₂ consumption in agricultural systems (Hall *et al.*, 1996). After including a canopy reduction factor (NO₂ deposition on foliage at night and diffusion through stomata during the day), the latter two estimates were 5.5 (\pm 2.2) (Yienger and Levy, 1995) and 9.0 Tg NO_x-N (Hudman *et al.*, 2012). Using the canopy reduction value of Yienger & Levy (1995), the annual estimate by Davidson & Kingerlee (1997) was lowered to 13 Tg NO_x-N. Annual modeled soil NO emissions for the United States (U.S.) were 0.37 Tg NO_x-N (without canopy reduction), as estimated by Yienger & Levy (1995), similar to an earlier estimate of 0.31 Tg NO_x-N by Williams et al. (1992a). Jaeglé et al. (2005) reported U.S. soil NOx emissions of 0.86 (\pm 0.60) Tg NO_x-N by using remotely sensed observations of NO₂ to adjust the bottom-up estimates, as discussed in detail below.

In a meta-analysis comprising data from 189 studies in agricultural fields and 210 under natural vegetation, global NO_x emissions from fertilizer N applications to cropland (including agricultural systems and managed grassland) were 1.8 Tg NO_x-N with a 95%-confidence interval of -80% and +406% (Stehfest and Bouwman, 2006). A statistical model based on 94 studies yielded global annual emissions of 0.67 Tg NO_x-N from agricultural soil (Aneja *et al.*, 2021).

The Yienger & Levy (1995) model is a semi-mechanistic, empirical model that has been widely used, modified, and updated for the modeling of global and regional soil NO_x emissions. For agricultural soil, an emission factor (EF; percentage of applied fertilizer N emitted as NO_x-N) of 2.5% (approx. 1.8% after subtraction of the canopy reduction effect), in addition to baseline emissions as in grassland (mean of published values; 10.9 g N ha⁻¹ d⁻¹) was used. For the nonagricultural biomes (desert, tundra, grassland, woodland, deciduous forests, coniferous forests, drought-deciduous forests), the mean NO flux of average fluxes determined in published studies was used, and these fluxes were adjusted for soil moisture ("wet" if at least 1 cm rain occurred in preceding two weeks, "dry" if such rain events had not occurred), temperature, and canopy reduction effects. Pulses of enhanced NO_x emissions were modeled if precipitation on dry soil occurred, and the magnitude (up to 15x of baseline emissions) and period of emission declines (days) of the pulse depended on the amount of rainfall (Davidson, 1992a, b; Williams et al., 1992b). The temperature effect in wet soils was linear from 0-10°C, exponential from 10-30°C, and "optimal" at temperatures >30°C (no further increase of flux with increasing temperature). For "dry" soils, mean NO_x flux values from the literature (e.g. Anderson & Levine, 1987; Stocker et al., 1993) were assumed, and the temperature effect was linear from 0-30°C. The canopy reduction effects were computed from the leaf area and the stomatal area indices and constants derived from the literature (Barbour et al., 1987; Jacob and Wofsy, 1990; Larcher, 1991). The country-specific monthly N fertilizer application rates and the global agricultural land area of 1.75x10¹³ m² were obtained from the Food & Agriculture Organization of the United Nations (FAO). The biomes were mapped on a 1°x 1° grid. As an estimate of the global estimate's uncertainty, the authors suggested 3.3 Tg NO_x-N, the calculated pre-industrial emissions, as the lower limit and 10.2 Tg NO_x-N, the emissions calculated without canopy reduction factor, as the upper bound.

The *Carnegie-Ames-Stanford (CASA) Biosphere* model, with a monthly time step, estimated annual global NO and N₂O emissions based on predicted N mineralization rates, soil moisture, temperature, soil texture, and microbial turnover (Potter *et al.*, 1996). Applications of synthetic N were not included in this model. Two percent of the N mineralized was assumed to be emitted as gaseous N (Keller *et al.*, 1988; Eichner, 1990), and a response function to water-filled pore space (WFPS) was used to determine relative proportions of trace gas species (NO, N₂O, N₂). The water-filled pore space (WFPS) was based on FAO soil texture classes and monthly precipitation. For temperate grassland, mean annual emissions were 0.4 kg NO-N ha⁻¹ and 0.2 kg N₂O-N ha⁻¹, and for cultivated land (without fertilizer applications), 1.5 kg NO-N ha⁻¹ and 0.8 kg N₂O-N ha⁻¹. Thus, the N₂O:NO ratio was 0.4 for temperate grasslands and 0.5 for cultivated land.

Elements of the CASA model were used to partition gaseous emissions within the *Integrated Model for the Assessment of the Global Environment (IMAGE)*, a conceptual model for the analysis of annual flows of total N (Van Drecht *et al.*, 2003; Wang *et al.*, 2017). Almaraz *et al.* (2018) estimated N surplus in California's cropland as the balance of N deposition, N fixation, N fertilizer, and N in irrigation water minus crop harvest N removal and NH₃ volatilization. The surplus N was then partitioned between leaching and gaseous emissions based on parameters temperature, water inputs, evapotranspiration, and edaphic properties, but the researchers did not elaborate on how these input variables were used, particularly in irrigated cropping systems. The researchers further partitioned the gaseous emissions into NO, N₂O, and N₂ by use of an index of water-filled pore space (WFPS) based on empirical findings by Davidson (1993) as in the CASA model (Potter *et al.*, 1996). The IMAGE model considers nitrate as the substrate and denitrification as the source of NO although most NO_x emitted from soil is a by-product of nitrification, which requires ammonium as substrate. It seems therefore unlikely that the model, without considering N dynamics of organic N, ammonium, and nitrate, can reliably predict soil NO_x emissions. In a letter to the journal where the Almaraz et al. (2018) study was published (Science Advances), Zhu-Barker et al. (2018) critiqued the lack of transparency in how model inputs were implemented, noting that this lack of detail makes a thorough evaluation of this IMAGE model implementation difficult, if not impossible. Both Maaz et al. (2018) and Zhu-Barker et al. (2018) disagreed with the extrapolation of short-term measurements (days to weeks) of NO_x fluxes to annual emission estimates that Almaraz et al. (2018) appeared to have performed in order to compare the measured with the modeled values. In rebuttals to Zhu-Barker et al. (2018) and Maaz et al. (2018), the authors affirmed their use of extrapolation of short-term measurements to annual emissions as validation of the model results (reported as annual emissions) and pointed to the NO_x emissions data collected by aircraft (discussed below under Trousdell et al. 2019) that were used for validation (Almaraz et al. 2018b; 2018c). Using the above approach, Almaraz *et al.* (2018) estimated California annual soil NO_x-N emissions as 161 Gg NO_x-N, with cropland accounting for 79% of these emissions and a mean NO_x flux of 19.8 kg NO_x-N ha⁻¹ yr⁻¹.

Kleeman et al. (2019) modeled reactive N (principally NO, NO₂, and particulate nitrate) concentrations in January 2010, 2013, and 2015 based on CARB inventory values (at that time without soil NO_x emissions) and compared results to measurements at ground-based monitoring sites in the SJV. The simulations were carried out using the *University of California Davis/ Institute of Technology (UCD/CIT)* model that predicts the evolution of gas and particle phase pollutants in the atmosphere in the presence of emissions, transport, deposition, chemical reactions and phase change. The simulations under-predicted measured concentrations of reactive N in the San Joaquin Valley, and the under-predictions appeared to be getting more severe with years passed. This trend was consistent with the presence of an unaccounted-for source of NO_x while NO_x emissions from mobile sources were decreasing. Inclusion of soil NO_x emission values modeled by the Almaraz et al. (2018) implementation of the *IMAGE* model generally increased predicted PM_{2.5} nitrate in January 2010, 2013, and 2015 and helped correct the under-prediction of PM_{2.5} concentrations. The study results implied the existence of an additional NO_x source in the SJV, and Kleeman et al. (2019) recommended measurements of soil NO_x emissions in the SJV to test the hypothesis that soil NO_x is this source.

Stehfest & Bouwman (2006) used a statistical approach in summarizing 189 measurements of NO flux from agricultural fields and 210 from soils under natural vegetation. They generated an annual worldwide estimate of 1.4 Tg NO-N from fertilized cropland and 0.4 Tg NO-N from grassland (managed grassland in mixed agricultural systems, excluding pastoral systems). The mean EF of 0.55% was calculated as a percentage of applied N (NO from fertilized minus that from unfertilized replicates) emitted as NO-N during experiments lasting >300 days. The factors N application rate, soil N content, climate, and length of experiment had significant effects on the emissions. The researchers acknowledged that NO emission estimates, especially from some natural systems, are highly uncertain due to the sparsity of data.

Steinkamp & Lawrence (2011) compiled results of 583 field measurements from 112 publications and modeled emissions with an updated version of Y&L, named *YL95EMAC*. Steinkamp & Lawrence (2011) estimated global annual emissions as 3.13 Tg NO_x-N from fertilized agricultural land based on the 583 published measurements. The mean measured NO fluxes and uncertainty ranges in different ecosystems in Steinkamp & Lawrence (2011)'s literature compilation was as

follows (g NO_x-N ha⁻¹ h⁻¹): Agriculture 0.18 (0.03-1.2); grassland 0.14 (0.02-0.9); woodland 0.24 (0.02-2.8); deciduous forest 0.04 (0.01-0.2); coniferous forest 0.23 (0.04-1.2).

Current estimation methods and many models for NO_x emissions from agricultural soil typically employ an emissions factor approach, calculating NO release based on fertilizer application rates. Steinkamp & Lawrence (2011) found a fertilizer-induced emission factor (FIE) of 1 (\pm 2.1) %, whereas Liu et al. (2017) reported an EF of 1.16%, with a 95% confidence interval of 0.71-1.61% and mean annual emissions of 4.1 kg NO-N ha⁻¹ yr⁻¹ in a global meta-analysis encompassing 520 field measurements in 114 publications. Stehfest & Bouwman (2006) determined a FIE of 0.55 in their meta-analysis based on experiments that lasted >300 days. Even lower EFs were computed based on the DNDC model results for California soils (0.39%) (Guo *et al.*, 2020). The global emission factor derived from the ratio of total soil NO_x emissions (12 Tg N yr⁻¹) to overall soil N turnover (1200 Tg N yr⁻¹) (Schlesinger and Bernhardt, 2020) approximates 1%.

The statistical model NO STAT was recently developed based on soil characteristics and fertilizer applications with particular attention to future emission scenarios through 2050 (Aneja et al., 2021). Accurately quantifying global NO emissions presents significant challenges due to their spatial and temporal variability. Recent research has expanded our understanding of various reactive N compounds' emissions from agricultural systems. The new statistical model is more accurate than an emissions factor approach for predicting NO emissions. The improved statistical model NO STAT offers new opportunities to predict and manage NO emissions in a changing climate (Aneja et al., 2021). This model incorporates data from various global agricultural systems and compares results with existing emission inventories like the Emissions Database for Global Atmospheric Research (EDGAR v.4.3.2), providing valuable insights for future environmental management strategies. The statistical model was developed using a multiple linear regression between NO emissions from global agricultural soils (obtained from the published scientific literature) and the physicochemical variables. The model was evaluated for 2012 NO emissions. In comparison to other data sets, the model provides a lower global NO estimate by 59% (NO STAT: 0.67 Tg N yr⁻¹; EDGAR: 1.62 Tg N yr⁻¹) (Aneja et al., 2021). The statistical model captures the spatial distribution of global NO emissions by utilizing a more simplified approach than those used previously. The NO₂ emission from agricultural soil is negligible, so this paper focuses on the emission of NO to generate a global map for NO emissions. Figure 13 gives the spatial distribution of global NO emission from agricultural soils calculated using NO STAT in kg N yr⁻¹ grid cell⁻¹ (Aneja *et al.*, 2021). The resolution of this map is five arc-minute, which is equivalent to about 8500 ha at the equator.



Figure 13. Comparison between the results from (a) NO_STAT, (b) EDGAR, and (c) absolute difference between the two models (Mg N yr⁻¹ grid cell⁻¹) (Aneja *et al.*, 2021).

Hudman et al. (2012) implemented the Berkeley-Dalhousie Soil Nitric Oxide Parameterization (BDSNP) for the year 2006 in GEOS-Chem, a global 3-D model of atmospheric chemistry driven by meteorological inputs from the National Aeronautics and Space Administration (NASA) Goddard Earth Observing System (GEOS). The approach of BDSNP was similar to that in Yienger & Levy's (1995) model, but soil moisture and temperature values were decoupled as fixed model inputs, and the NO_x response to different soil moisture and temperatures was allowed on a continuum. Furthermore, the NO_x emission pulsing length and strength were modified to depend on the duration of the antecedent dry period and the soil moisture history rather than precipitation amounts. Further changes included the inclusion of other N-compounds (NH₃, ammonium, nitrate, HNO₃, NO₂, and peroxyacetyl nitrate) as wet and dry deposition; and updated N fertilizer and manure input representation valid for the year 2000 (Potter et al., 2010). The BDSNP model mimicked fertilizer application timing by adding 75% of the annual fertilization in the first month and the rest over the remainder of the growing season. Of the 10.7 Tg NO_x-N global annual soil NO_x emissions (without canopy reduction), 1.8 Tg N was predicted from fertilizer N inputs and 0.5 Tg N from atmospheric deposition. For agricultural soils, a 1.5% emission factor (EF, percentage of applied fertilizer, and manure N emitted as NO) was chosen in order to match the total global soil NO emissions found in Stehfest & Bouwman's (2006) meta-analysis. Emission estimates for different biomes were adopted from Steinkamp & Lawrence (2011).

Rasool et al. (2019) modeled soil nitrogenous emissions in natural and agricultural systems within the *Community Multiscale Air Quality (CMAQ)* model v5.1, which considers NO_x emissions from all sources, as well as atmospheric transport and transformation of NO_x. CMAQ is the U.S. EPA's widely used open-source regional air quality model. The mechanistic representation of nitrogenous emissions from soil included some notable refinements compared to the Yienger & Levi (1995) and BDSNP models. First, for both agricultural and non-agricultural soil, nitrification and denitrification were modeled in a DayCent (Parton *et al.*, 2001) sub-model that uses the Environmental Policy Integrated Climate (EPIC) model, which includes fertilizer N applications and wet and dry deposition, to predict N availability for nitrogenous emissions (Figure 14). Second, the DayCent sub-model partitioned NO_x and N₂O based on relative gas diffusivity in soil. Third, in addition to NO, N₂O, and NH₃, the CMAQ model predicted HONO emissions based on the ratios of emitted HONO:NO in 17 ecosystems (Oswald *et al.*, 2013), and a WFPS adjustment factor was used to modulate this ratio as follows: HONO emissions increased with increasing soil moisture up to 10% WFPS and then decreased until they were negligible around 40% WFPS (Su *et al.*, 2011; Oswald *et al.*, 2013). The following algorithms were similar to the earlier models: The biome classification (each with a specific base emission factor) was according to Steinkamp & Lawrence (2011). The canopy reduction factor of NO₂ was calculated according to formulations by Wang et al. (1998). The pulsing term depended on the length of the dry period and the change in soil moisture.



Figure 14. Mechanistic scheme of soil nitrogenous emission as implemented in CMAQv.5.1 by Rasool *et al.* (2019).

Rasool et al. (2019) compared modeled tropospheric NO_2 concentrations with those observed by the Ozone Monitoring Instrument (OMI standard product V. 4.0) on board the Aura satellite, in

operation since 2004, with a ground resolution of 13km x 25km, observed densities of total column NO₂, of which the troposphere contributes 20%-30% (Lamsal et al., 2021). The uncertainty of OMI observations for NO2 is ~35% (Boersma et al., 2011; Bucsela et al., 2013; Lamsal et al., 2021). The CMAQ model (v. 5.1) under-predicted NO₂ density for May 2011 by 5.1% for California (excluding the Imperial Valley due to grid location) relative to OMI NO₂ column densities (underpredictions by Y&L95 and BDSNP were 18.6 and 17%, respectively) (Rasool et al., 2019). For July 2011, the underprediction for California by CMAQ was 19% (17.4 and 11.5% for Y&L95 and BDSNP) (Rasool et al., 2019). The NO emission rates with this scheme were up to a factor of 1.5 higher than those by Y&L95 but not by as much as those by BDSNP (Hudman et al., 2012). The modeled hourly average soil NO_x emission rates in the Central Valley in May and July 2011 according to Rasool et al. (2019) were between about <0.1 - 0.7 g NO_x-N ha⁻¹ for the CMAQ v.5.1 parameterization vs. <0.1 - 1.1 g NO_x-N ha⁻¹ for the BDNSP and <0.1 - 0.7 g NO_x-N for the Yienger & Levy parameterizations. The percentage of soil NO_x to total NO_x aggregated across the CONUS domain varied from 10 - 13% for the months of May and July 2011 with CMAQ vs. the Y&L95 model, which yielded 15 - 20 % for soil NO_x, and the BDSNP scheme, which yielded 20-33% (Rasool et al., 2019) (Table 1).

The Biogenic Emission Inventory System (BEIS) model, which operates within CMAQ, estimates the timing and spatial distribution of soil NO_x emissions, as well as the interactions of those emissions with air quality and meteorology. BEIS, developed by the U.S. EPA, estimates NO emissions from soils at a spatial resolution of 1 km. According to the EPA, the combination of BEIS and CMAQ (current versions) represents the state of the science for estimating soil NO_x. The BEIS model uses the EPIC biochemical model for representation of the soil N pool at a daily time-step and implemented with CMAQ, enables updates to use year- and location-specific N fertilizer data. The cropland information is from EPA's Biogenic Emissions Landcover Database version 6 (BELD6). A limitation of the modeling scheme for California is the soil moisture parameter, which does not account for irrigation. The soil moisture model input is generated by WRF-Chem. The BEIS considers the growing season to last from April 1 to October 31. Outside the growing season and in non-agricultural land, NO emissions are estimated based on temperature and a grassland emission factor only. The Model of Emissions of Gases and Aerosols from Nature (MEGAN) is another available state-of-the-science option in the CMAQ modeling system. MEGAN employs similar soil NOx science but also lacks irrigation schedules in its algorithms for estimating soil NO_x. The BEIS modeling results inform EPA's National Emissions Inventory (NEI).

In California, CARB's *California Emissions Projection Analysis Model (CEPAM)* predicts soil NO_x emissions based on the mechanistic biogeochemical DeNitrification-DeComposition (DNDC) model. DNDC uses similar inputs as the DayCent sub-model Rasool et al. (2019). employed in CMAQ to simulate NO emissions (Guo *et al.*, 2020). The DNDC model can predict C and N dynamics, including the production of CO₂, CH₄, N₂O, N₂, NO, and NH₃, in daily time steps. DNDC has not been widely used to simulate NO flux. In one other application, the researchers noted that in comparison with measured NO fluxes, DNDC captured the differences in the magnitude of NO emissions among some of the sites (Butterbach-Bahl et al. 2009). However, at other sites, the model under- or over-estimated emissions (by up to a factor of 4) (Butterbach-Bahl *et al.*, 2018a; Deng *et al.*, 2018b). The researchers adopted the land use, soil properties, crop management, and soil environment/meteorology data of that calibration. Additionally, canopy reduction factors were applied in post-model processing (Rasool *et al.*, 2019). The model was also

calibrated for urban land (lawns) and dairy forage production land. Simulations were carried out for all of California for the year 2013, including the following land use categories: Cropland, urban, forest, grassland, shrubland, and fallow (Guo et al., 2020). The model predicted annual soil emissions of 2,643 Mg NO_x-N (2.6 Gg N), with a daily mean of 7.2 Mg NO_x-N d⁻¹, for the entire state of California. The uncertainties of the model were estimated by varying the most sensitive model parameters, i.e., soil organic C levels (0.67% - 1.69% C), fertilizer type (nitrate vs. ammonium), and irrigation methods (flood/furrow, sprinkler, surface drip, sub-surface drip), and modeling these scenarios produced an estimated range of 1,529 to 5,532 Mg NOx-N (1.5 to 5.5 Gg N) for statewide annual emissions. The researchers compared the modeled seasonal NO_x emissions with the soil NO_x emissions of 15 data sets of measured fluxes in the same type of cropping systems and under the same environmental conditions as specified in the model via linear regression. However, the data sets of the measured fluxes were temporally too sparse to allow estimates of seasonal emissions that could be used as validation of the modeling results. Therefore, the estimates generated by this configuration of the DNDC model cannot be considered validated. A comparison of NO_x emissions between NEI and CEPAM inventories is shown in Table 5 for the eight counties of the SJV and Imperial County, as well as California as a whole.

Table 5. Average daily total NO_x emissions, soil NO_x (sNO_x) emissions, and the ratio of sNO_x /total NO_x in the San Joaquin Valley (San Joaquin, Fresno, Tulare, Kern, Madera, Merced, Stanislaus, and Kings counties), Imperial County, and all of California in the NEI and CEPAM inventories in 2020.

	NEI			CEPAM		
Region	Total NO _x	sNO _x	sNO _x /total NO _x	Total NO _x	sNO _x	sNO _x /total NO _x
	tons NO	$D_2 d^{-1}$	%	tons NC	$D_2 d^{-1}$	%
San Joaquin Valley	293	31.9	10.9	239	9.7	4.1
Imperial County	17.2	2.6	15.4	16.2	0.9	5.5
Statewide	1,429	110.4	7.7	1,405	25.8	1.8

To help constrain the large uncertainties of bottom-up estimates of NO_x surface-to-atmosphere fluxes, Martin et al. (2003) combined (top-down) space-based observations of NO₂ concentrations in the troposphere with bottom-up modeling outcomes. The researchers used NO₂ vertical column density data observed by the Global Ozone Monitoring Experiment (GOME), from September 1996 – August 1997 to derive monthly estimates of total NO_x emission through modeling with GEOS-CHEM v.4.26. The GOME instrument observed the atmosphere with a spatial resolution of 40 x 320 km, achieving global coverage every three days. For each location and month, the authors combined the top-down NO₂ emission stimates (derived from GOME observations) and the bottom-up estimates of NO_x emissions from the different sources of NO_x (fuel combustion, biomass burning, soils) and the respective relative (geometric) errors of each NO_x source to generate *a posteriori* estimates of NO_x emissions and errors (Martin *et al.*, 2003). For each location, the *a priori* soil NO_x emissions were computed using a modified version of Yienger & Levy's

(1995) model. The top-down and bottom-up estimates were mathematically combined by weighting the bottom-up *a priori* emissions with the variance of the top-down emissions and vice-versa to yield the *a posteriori* emissions with the lowest possible error. (equations 7-9).

The variance of the weighted sum $x^2(ln\varepsilon_a)^2 + (1-x)^2(ln\varepsilon_t)^2$ is minimized by

$$x = \frac{(ln\varepsilon_a)^2}{(ln\varepsilon_t)^2 + (ln\varepsilon_a)^2} \text{ and } 1 - x = \frac{(ln\varepsilon_t)^2}{(ln\varepsilon_t)^2 + (ln\varepsilon_a)^2}$$
(7)

where x and 1-x are weights of relative errors of bottom-up $(ln\varepsilon_a)$ and relative errors of top-down $(ln\varepsilon_t)$ emissions, respectively. The minimum-variance weighted sum of the emissions E is

$$lnE = \frac{(lnE_t)(ln\varepsilon_a)^2 + (lnE_a)(ln\varepsilon_t)^2}{(ln\varepsilon_t)^2 + (ln\varepsilon_a)^2}$$
(8)

where E_t are mean top-down and E_a mean bottom-up emissions, and

$$(ln\varepsilon)^{-2} = (ln\varepsilon_t)^{-2} + (ln\varepsilon_a)^{-2}$$
(9)

By design, the *a posteriori* estimates of the soil NO_x emissions depend on the *a priori* values. The *a posteriori* soil NO_x emission estimate was greater than the *a priori* one for the Western U.S. in summer, which suggests that the soil NO_x emissions estimate, as predicted by the Yienger & Levy 1995 model, was too low (Martin *et al.*, 2003).

Jaeglé et al. (2005) also found that the *a priori* global soil NO_x emissions, according to Yienger & Levy (1995), with a modified canopy reduction factor of about 20% (Wang *et al.*, 1998), were lower than those based on NO₂ observations by GOME. The researchers partitioned the sources of the remotely sensed NO₂ columns observed by GOME in January, April, June, and August 2000 among fuel combustion (fossil fuel and biofuel), biomass burning, and soils by using information on the locations where fuel combustion dominates as NO₂ source and information on the spatiotemporal distribution of remotely sensed fires (biomass burning). To create the *a posteriori* estimates, the researchers combined the top-down and the bottom-up inventories and their relative errors, as shown above (Martin *et al.*, 2003). Combining the top-down NO_x emission inventory and its errors with the bottom-up estimates and associated errors lowered the overall uncertainty of the *a posteriori* NO_x emission estimates from a factor 3 to a factor 2. In the U.S., for the year 2000, the posteriori annual soil NO_x emissions were 0.86 (relative error $\pm 70\%$) Tg NO_x-N. Globally, Jaeglé et al. (2005) estimated soil emissions to contribute 22% of total NO_x emissions vs. 14% as calculated by Yienger & Levy (1995). Validations of the model were not carried out for any California region. The estimates based on the remotely sensed NO₂ column data were larger than the *a priori* estimates and suggested that the modified Yienger & Levy (1995) model may have underestimated soil NO_x emissions and/or that potential other sources of NO_2 were not accounted for. The approach of combining top-down and bottom-up estimates of NO_x emissions could be used to narrow the uncertainty of soil NO_x emissions estimates when both bottom-up data and top-down values obtained by remote sensing are available for a region or air basin.

Vinken et al. (2014) calculated top-down constraints on *a priori* modeled soil NO_x emissions in 11 regions of the world where soil NO_x dominates overall NO_x emissions, such as the Sahel in Africa and in the U.S. the Upper Midwest (May-September) for the year 2005. In these regions, strong correlations between modeled soil NO_x emissions and tropospheric column NO₂ mass confirmed that the patterns of NO₂ columns reflected soil NO_x emissions. For modeling, GEOS-Chem v.9-021 parameterized with BDSNP was used. Subsequently, the researchers constrained the modeled NO₂ columns with OMI top-down observations using a mass balance approach. In most regions, the modeled NO₂ column amounts were lower than the remotely sensed ones, on average by 35%, and modeled NO₂ by ground-based monitors and modeled NO₂ concentrations adjusted by the OMI observations. With this increase of 35% in the 11 regions of the world, the global inventory was 10 Tg NO_x-N yr⁻¹. If this adjustment was extrapolated to all modeled NO_x emissions, the global estimate was 12.9 (\pm 3.9) Tg N yr⁻¹.

Sha et al. (2021) made the following changes to the BDSNP parameterization: Assumed soil temperature the one at the soil surface instead of that 2 m above it; updated land cover data; assumed an EF of 2.5% for fertilized fields and adopted the N fertilizer scheme from Hudman et al. (2012) which assumed that 75% of annual fertilizer is applied at planting and 25% during the growing season and a 'decay lifetime' of four months for fertilizer N. The researchers called this modified model version Berkeley Dalhousie Iowa Soil Nitric Oxide Parameterization (BDISNP). The soil NO_x emissions modeled by BDISNP for July 2018 were 13.4 Gg NO_x-N/month for all of California's soils and 3.6 Gg NO_x-N/month for California's cropland (Table 6). Earlier, Almaraz et al. (2018) had determined the same value – 161 Tg NO_x-N yr⁻¹, which equates to 13.4 Tg NO_x-N month⁻¹ – as an estimate of California's total soil NO_x emissions. In comparison, BDSNP predicted 14.35 Gg N/month (+0.95 Gg N/month more than BDISNP) for soil NO_x in all of California (Sha et al. 2021, not shown). Based on the simulated total NO_x emissions of 33.5 Gg N/month, the contribution of soil NO_x to total NO_x emissions would be 40%. Table 6 also shows total and soil NO_x emissions for 2011 and 2020, as reported by NEI and CEPAM. According to NEI and CEPAM, soil NO_x emissions contributed 5.8-7.7% and 1.8-2.2% to total NO_x emissions in the state, respectively.

	Year	Total NO _x emissions	Soil NO _x emissions	Soil NO _x as % of total NO _x emissions
		Gg N/month	Gg N/month	Gg N/month
Sha et al. (2021)	2018	33.5	13.4	40.0
U.S. EPA 2011	2011	18.02	1.05	5.8
U.S. EPA 2020	2020	12.02	0.925	7.7

Table 6. Average California total NO_x and soil NO_x emissions in July 2018 (Sha et al., 2021) and average monthly emissions in EPA and CARB inventories.

CARB 2011	2011	15.35	0.28	1.8
CARB 2020	2020	10.1	0.22	2.2

The monthly mean NO₂ tropospheric column densities for July 2018, modeled by BDISNP, were lower than those observed by the TROPOspheric Monitoring Instrument (TROPOMI) aboard the European Space Agency Sentinel-5 Precursor satellite (Table 7).

Table 7. Mean vertical column densities observed by TROPOMI and modeled by BDISNP and MEGANv.2.04 for July 2018 and TROPOMI uncertainty (Sha et al. 2021; S5P-MPC-KNMI-PRF-NO₂; van Geffen et al. 2020).

Instrument/Model	All CA	CA cropland	Random error troposphere	Random error stratosphere
		molecules cm ⁻²		
TROPOMI	1.4 x 10 ¹⁵	1.9 x 10 ¹⁵	$0.5 \ge 10^{15}$	$0.7 \ge 10^{15}$
BDISNP	0.94 x 10 ¹⁵	1.7 x 10 ¹⁵		
MEGANv.2.04	0.75 x 10 ¹⁵	1.2 x 10 ¹⁵		

Both the BDISNP and MEGAN modelling results were lower than, but within the uncertainty of TROPOMI observations. The mean bias of BDISNP compared to TROPOMI observations was - 39.8%. Column density values modeled by MEGAN v.2.04 had a mean bias of -52% compared to TROPOMI observations. The researchers imported the values for anthropogenic emissions from the U.S. EPA's National Emission Inventory (NEI) 2011. Sha et al. (2021) also demonstrated that BDISNP was able to predict a pulsed NO_x emission event due to rainfall in shrubland in southern California by comparing model results with ground-based measurements by EPA monitoring stations, which picked up the spike of NO_x due to the wet-up.

Zhu et al. (2023) partitioned the sources of NO_x in a part of the San Joaquin Valley based on multivariate regression analysis of NO_x emission data collected by aircraft and land cover maps. The researchers conducted six flights on weekdays over the area between Bakersfield and Fresno in June (6/1-6/22/2021) and measured NO_2 mixing ratios within the boundary layer using eddy covariance techniques. NO_x fluxes were calculated based on the height of measurements, vertical and horizontal wind speed, wind direction, boundary layer height, surface roughness length, and friction velocity. Airborne fluxes were extrapolated to surface flux by accounting for divergence. A footprint map at the spatial resolution of 500m x 500m was aligned with the geographic coordinate space of each flux observation. The USDA CropScape database (2018) and a national highway map were used to assign one of three types of land cover – urban, highway, cropland – if a land type made up more than 50% of a 4kmx4km grid cell or for 'Highway' if a highway ran through a grid cell. Highways included 37% of flux observations, urban 23%, and cropland type (including grassland) 96%. About two-thirds of the fluxes' footprint extents were within 3km (range 0.16-12km) of the aircraft flight track. The average uncertainty of the data within the 500x500m cells was 60% based on random errors due to the instrument, turbulence noise (25%), lag time correction (25%), and boundary layer heights (30%). The median observed weekday fluxes in this part of the San Joaquin Valley were 2.6 (range of 1.4 - 4.6) g NO_x-N ha⁻¹ h⁻¹. Then, the fluxes were disaggregated into the three land cover types using multivariate regression combined with the footprint distribution of the land cover types (Hutjes *et al.*, 2010). Table 8 compares the emission rates derived in this study with those of CARB's Emission Factor (EMFAC) scheme, as well as the results of modeling by MEGANv.3, BEIS, and BDISNP.

Table 8. Medians and inter-quartile ranges of NO_x emissions in the San Joaquin Valley between Bakersfield and Visalia from different sources as observed in this study and as estimated by EMFAC, MEGANV.3, BEIS v.3.14, and BDISNP.

Source	Zhu et al. 2023	EMFAC	MEGAN	BEIS	BDISNP
			g NO _x -N ha ⁻¹ h ⁻¹		
Highway	3.5 (1.4 - 4.7)	1.2 (0.5 - 1.6)			
Urban	3.7 (1.4 - 5.8)	4.5 (1.3 - 6.1)			
Cropland	3.0 (1.4 - 4.5)		0.15 (0.1-0.2)	0.15 (0.1-0.2)	1.7 (1.1 -2.0)

As determined by Zhu et al. (2023), the highway emissions were about three times higher than the emissions from mobile sources reported by EMFAC. The soil NO_x emissions estimated by MEGANv.3 and Biogenic Emission Inventory System (BEIS) used by the U.S. EPA were lower by at least an order of magnitude than those found in Zhu et al. (2023)' study, and soil NO_x fluxes modeled by BDISNP were about half as great as the ones in Zhu et al. (2023) study. The study supports the models and estimates that predict higher soil NO_x emissions than those in the currently used inventories by CARB and U.S. EPA, but this research did not improve the uncertainty of soil NO_x emission estimates. The uncertainty of the NO_x emissions from each source was large, and the researchers reported only medians and interquartile ranges (Table 8). An analysis in this study showed that overall soil NO_x fluxes estimated by BDISNP were about 2.2 times lower (regression with r=0.52) compared to this study's estimated soil NO_x fluxes, but Sha et al. (2021) estimated the contribution of soil NO_x to total NO_x emissions to be 40% according to BDSINP modeling, which suggests that the soil NO_x contribution to total NO_x estimated in this study is even higher. It also appears that mobile sources of NO_x in the San Joaquin Valley may have been higher than estimated in CARB's inventory. A potential concern regarding the study's results and methodology might be that NO_x from mobile/urban sources may have had an unintended impact on the fraction attributed to soil NO_x emissions although an important factor, NO_x emissions from off-road vehicles, was filtered out prior to the calculations of soil NO_x fluxes. Whether there was interference on soil NO_x emissions from mobile/urban sources might have been detected from a comparison of weekend and weekday NOx emissions since sources from urban/mobile sources are known to be lower on weekends than on weekdays (Russell et al. 2010; Goldberg et al., 2021; Wang et al., 2023), whereas soil NO_x emissions would not vary significantly between weekdays and weekends. However, Zhu et al. (2023) did not present the results of weekend observations.

In approximately the same part of the San Joaquin Valley as the one where Zhu et al. (2023) conducted their campaign in June 2021, total NO_x emissions had been estimated earlier, in July/August 2016, based on six days of flight data covering most of the area (720,000 ha) of Fresno, Tulare, and Kings counties (total of 971,200 ha) (Almaraz et al., 2018; Trousdell et al., 2019) The mean NO_x emissions for the six flights was 216 Mg NO_x d⁻¹ with a standard error of the mean of 33 Mg NO_x d⁻¹ based on the variability among the six emission estimates (Trousdell *et al.*, 2019). Earlier, Almaraz et al. (2018) reported an emission estimate of 190 (±130) Mg NO_x d⁻¹ for the same flight data. The anthropogenic emissions for this region, according to CEPAM, were 104 Mg NO_x d⁻¹ (Trousdell *et al.*, 2019), and therefore, based on the mean total NO_x emission estimate, soil NO_x emissions would be >100 Mg NO_x d⁻¹ with the lower bounds of the biogenic NO_x emissions 79 Mg NO_x d⁻¹ (corresponding to approximately 1.35 g NO_x-N ha⁻¹ h⁻¹) from agricultural land of these three counties (Trousdell et al., 2019). However, the CEPAM inventory lists biogenic emissions at only 5.6 Mg NO_x d⁻¹. The mean standard deviation calculated as the mean of each flight's relative error was 187 Mg NO_x d^{-1} (Trousdell et al. 2019). Therefore, if the mean of the standard deviations comprising the error terms of the individual flights were considered as uncertainty, the mean biogenic emissions would be 112 (with a confidence interval of -75 to +300) Mg NO_x d⁻¹ and the physically realistic lower bound zero.

Apportioning total NO_x emissions to different sources is a core challenge when estimating soil NO_x emission data by indirect methods. The U.S. EPA has reported reductions in overall NO_x emissions of -5.9% yr⁻¹ for the U.S. between 2005 and 2017. According to the NEI, the overall decrease was due to the decrease in anthropogenic emissions, but these emissions accounted only for 61% in 2005 and 42% in 2017 (Silvern et al., 2019). Therefore, natural emissions (lightning, biomass burning, soil) play a relatively increasing role as anthropogenic emissions decrease. Wang et al. (2023) analyzed California's NO_x emission trends from 2009-2020 by averaging NO₂ column densities observed by OMI and TROPOMI, as well as ground-based monitors, during summers (June-September) within each of the following land cover types: Urban (4%), forests (22.8%), croplands (9.5%), scrublands (including shrublands, savannas, grasslands; 48.4%), barren (15.3%). The land cover types were classified by MODIS (Moderate Resolution Imaging Spectroradiometer v.6). Also, meteorological and wildfire records were considered. Temperature and soil moisture functions were empirically fitted to the NO₂ column data in the different non-urban land cover types, and the BDSNP model was parameterized accordingly. Irrigation effects and mobile sources of NO_x within land cover types were not considered. The researchers then calculated the temperature- and soil moisture-driven changes in NO₂ column densities in each non-urban land cover type during 2009-2020 and proposed that these changes could be ascribed to soil NO_x emissions in the non-urban land cover types. Forests showed a significant increase of soil-derived NO₂ according to this analysis, croplands and barren lands showed slight increases. The trend analysis showed an increase of +4.2±1.2% yr⁻¹ for forest land and urban areas and a decrease of - $3.7\pm0.3\%$ yr⁻¹ (P<0.05), while NO₂ column trends in the other land cover types did not exhibit significant changes. In urban areas, the researchers found 42% lower emissions on weekends than on weekdays, among the non-urban land uses, only cropland showed a slight decrease in column densities on weekends (see also Goldberg et al. 2021). The researchers identified fire effects (biomass burning) as the strongest factor counteracting the decrease in urban land cover NO₂ between 2009 and 2020.

Validating satellite measurements with in-situ and ground-based measurements has been difficult because the spatial resolution of satellite measurements is too coarse (tens of km) to capture the

variability of NO₂ concentration exhibited by ground-based and in-situ measurements (Figure 15). Due to the relatively short (hours) lifetime of NO₂, this trace gas is usually confined to a local scale and shows high spatial and temporal variability. In 2013, NASA compared NO₂ column densities collected by instruments on the surface (Pandora spectrometer), aircraft (in-situ vertical spirals), and space (Ozone Monitoring Instrument, OMI, on the Aura satellite) during the DISCOVER-AQ campaign (Choi et al., 2020). The correlation between OMI (OMI_{SP}, standard product v.3.1) values and NO₂ columns derived from airborne measurements was high (r=0.77 - 0.81), but mean OMI_{SP} values were 54-57% lower than the NO2 columns derived from airborne measurements (Choi et al., 2020). The disagreement between the relatively large OMI pixel/footprint and ground and aircraft measurements with smaller footprints was likely due to, at least in part, the spatial variability of NO2. The distance between ground-based locations and locations where measurements by aircraft were made was within 5 km, and the spiraling aircraft covered an area with a diameter of about 2 km; the Ozone Monitoring Instrument (OMI) on board the Aura satellite observed NO₂ column density with a footprint of 13 x 24 km (near nadir) to 24 x 160 km (outermost edges of the swath) (Choi et al., 2020). Down-scaling OMI profiles brought the aircraft-derived and OMI mean values into closer agreement. Down-scaling referred to the spatial weighting of sub-pixel variability based on (CMAQ) modeling while the quantity (total number of molecules) of the satellite data over the pixel was preserved. After down-scaling the OMI data, the mean differences between OMI profiles and aircraft measurements were 7.6 to 14.2% (r=0.47-0.56). There was still considerable spatial variability between point measurements and remotely sensed pixels even after down-scaling OMI pixels. The differences between point measurements (Pandora) and down-scaled OMI profiles ranged from +3% to -54%, and the regression analysis correlation coefficients ranged from 0.2 to 0.97 (Choi et al., 2020).



Figure 15. Conceptual illustration of NO_2 observations at varying scales depending on the instruments used: Ground-based monitors measuring NO_2 mixing ratios at the surface, Pandora making direct-sun measurements of total column NO_2 , airborne instruments measuring in-situ NO_2 profiles, OMI aboard the satellite Aura observing total column and tropospheric column NO_2 densities.

During the same DISCOVER-AQ campaign in January/February 2013, Chen et al. (2020) compared vertical daytime distributions of NO₂ and other gases during aircraft flights between Bakersfield and Fresno and modeling results by WRF-Chem and CMAQv.5.0.2. The modeled NO_x concentrations at urban locations corresponded well with measurements by ground-based monitors at those locations, but the model underpredicted NO₂ concentrations at more rural sites (Shafter -52%, Tranquility -60%) compared to ground-based measurements. The under-prediction could be due to underestimation of the soil NO_x emissions or other sources of NO_x at these locations and, according to the authors, the spatial allocation of existing emissions or inadequate transport in the model.

Oikawa et al. (2015) combined NO flux measurements with modeling and then compared outcomes with remote sensing observations of NO₂ densities. The researchers measured soil NO emissions in response to N fertilization, rewetting, and temperature by soil cover method (direct measurement with flux chamber). In one experiment, a solution of ammonium nitrate (NH4NO3) was applied onto the soil surface of a sorghum field under standard fertilization (270 kg N ha⁻¹ year⁻¹) at the rate of 20 kg N ha⁻¹ before measurements started. Another experiment was carried out in a sorghum field that had not received N fertilizer for about five months. In that experiment, either 50 or 100 kg urea-N were side-dressed, followed by flood irrigation prior to NO flux measurements. The research was conducted at the California Desert Research and Extension Center, Holtville, CA, where soils are alluvial with 2.34% C, 0.13% N, and pH 8.3. Mean NO emissions across all experiments were 2.3 g N ha⁻¹ h⁻¹ with a median of 0.72 g N ha⁻¹ h⁻¹. Within 20 days of fertilization, mean emissions were 4.6 g NO-N ha⁻¹ h⁻¹. Several factors may have contributed to these high average fluxes: In the first experiment, nitrification was likely taking place near the soil surface where impediments to gas transport are low, leading to efflux rather than consumption of NO. The choice of fertilizers (NH₄NO₃, urea) (Liu *et al.*, 2017) and the relatively high soil pH, in addition to the high soil temperatures (reported as the average between temperatures at 2 and 10 cm depth) up to 40°C, were also conducive to high nitrification rates and NO production. Earlier, even higher average NO fluxes of approx. 8 g N ha⁻¹ h⁻¹ has been reported in the pre-plant season of a wheat production system fertilized with 187 kg urea-N ha⁻¹ in the Yaqui Valley, Sonora, Mexico (Panek et al. 2000; Matson et al. 1998). Oikawa et al. (2015) modeled surface NO₂ concentration with MEGANv.2.0 within WRF-Chemv.2.0 using the NO_x fluxes measured in the experiments. The researchers adjusted the default soil NO_x emission rates in the WRF-Chem v.2.0 model 10-fold to 0.72 g NO_x-N ha⁻¹ h⁻¹ (10x) to match the modeled NO_x fluxes with the median of all measured fluxes and to 4.64 g NO_x-N ha⁻¹ h⁻¹ (64.5x) to match the average of all measured fluxes within 20 days of N fertilizer applications and compared the thus simulated NO₂ mixing ratios to those measured at the El Centro-9th Street, CA air quality monitoring site during 7 days. This regression analysis yielded $r^2=0.44$ for WRF-Chem default and 10x and $r^2=0.42$ for the 64.5x simulation; root mean square errors (r.m.s.e) were 6.1 for default, 5.7 for 10x, and 9.5 for 64.5x. Although the model parameterization with 10x showed a slightly better fit than the default (and a worse fit for the 64.5x increase), this small improvement of the r.m.s.e. for the

10x parameterization in the regression analysis cannot be considered evidence that NO_x emission rates are an order of magnitude higher in the region surrounding the El Centro monitoring station. However, both the WRF-Chem default and the modeled 10x emission rate resulted in a lower tropospheric NO₂ column density (by -63% and -56%, respectively) compared to OMI observations (minimum footprint of 13x24 km), whereas the 64.5x emission rate did not. The OMI results imply that both the default and 10x (0.72 g NO_x-N ha⁻¹ h⁻¹) modeling results could be underestimated as the uncertainty of OMI observations was probably less than 63% and 56%. Irie et al. (2012) compared OMI observations with point measurements of full vertical column densities by multi-axis differential absorption spectroscopy in China and Japan and reported a bias of -10±14% for OMI. The NASA Goddard Earth Sciences Data and Information Services Center evaluated the OMIv3.1 and the newer v.4.0 during the DISCOVER field campaign 2013 in California and other states and found the site-specific average of OMI observations to be within 35% of Pandora results (Lamsal et al., 2021). In comparison of OMI observations with measurements by research aircraft during the DISCOVER campaign, there was generally a good correlation (r=0.77 - 0.83) but poor agreement of actual values. During the campaign, the average OMI observations were lower than aircraft observations by 38.8% with v.3.1 and 23.1% with v.4.0 (Lamsal et al., 2021).

Besides remote sensing, scientists have also used isotopic analysis of NO_2 in an agricultural area as a means to estimate the contribution of soil NO_x to total NO_x . Lieb et al. (2024) determined the contribution of soil NO_x to total NO_x through analysis of NO_2 isotope ratios in air samples collected monthly from June 2022 to April 2023 at two locations in the Salton Sea air basin. The air samples were taken at about 10 and 15 feet above the surface. The researchers used the method described by Blum et al. (2020) to determine isotope ratios of the air samples' NO_2 . To calculate the contribution of soil NO_x to total NO_x in the Salton Sea air basin, the following equation was used:

$$\delta_{obs} = \left[\left(E_{inv} * \Sigma_{a,b,c,s}^{i} \alpha_{i} * \delta_{i} \right) + E_{s} * \delta_{s} \right] / \left[E_{inv} + E_{s} \right]$$
(10)

where δ_{obs} is the mean $\delta^{15}N$ of the air samples, E_{inv} the total emissions (tons NO_x-N d⁻¹) in the CEPAM inventory for the Salton Sea air basin, α_i the fraction of each source (mobile, biomass burning, stationary, soil), δ_i the $\delta^{15}N$ signature of each source, and E_s the soil NO_x emissions (tons NO_x-N d⁻¹), to yield

$$E_s = \left[\left(\delta_{obs} - \Sigma_{a,b,c,s}^i * \alpha_i * \delta_i \right) * E_{inv} \right] / \left(\delta_s - d_{obs} \right)$$
(11)

The assumption was that the inventory emissions were correct regarding all sources but that there was an additional soil source () that impact the *N* of the total NO_x. The *N* of the other NO_x sources were assumed to be the means of published values in the literature. The *N* of the soil emissions (mean -33.2±9.6 ‰) was less enriched (i.e., lighter) than the other sources, although there was some overlap in the range of *N* with stationary sources (mean -16.5±1.7‰). Based on the above analysis, soil NO_x emissions contributed 11.4 (±4.9 tons NO_x per day, or on average, 27% of the total NO_x emitted in the Salton Sea Air Basin (Table *9*). According to this study, soil NO_x

emissions were, on average, a magnitude higher, and total NO_x was about 37% higher than in the CEPAM inventory. Since almost all NO_x analyzed was in the form of NO_2 , the NO_x estimate of Lieb et al. (2024) would include HONO as a source, if present. The mean isotopic signature of the NO_2 differed between the two sites (by about 5‰ on average), but the *N* values were for the most part consistently similar within each site.

G	GED () (T 1 1 0001
(mobile, biomass bu	urning, and stationary) and their percen	tage of total NO _x emissions.
on the isotopic signa	ature of each source and the inventory n	mean NO _x amounts for all other sources
Table 9. NO _x source	es for 2022 in the CEPAM inventory a	nd in the Lieb et al. (2024) study based

Source	CEPAM		Lieb et al. 2024		
	tons NO _x d ⁻¹	%	tons NO _x d ⁻¹	%	
Mobile	28.3	85.2	27.7	64.6	
Biomass burning	0.8	2.4	0.7	1.6	
Stationary	3.0	9.0	3.1	7.2	
Biogenic soil	1.0	3.0	11.4	26.6	
Total	33.2		42.9		

5.1 Conclusions NO_x emissions modeling

Table 1 shows the wide range of soil NO_x emissions modeling estimates. For many models, uncertainty ranges of the modeling results are either missing or could only be estimated by other means than statistics. For example, Yienger & Levy (1995) proposed the modeled pre-industrial emissions as lower and the modeled emissions without canopy reduction factor (CRF) as upper bounds, and for DNDC, the model's uncertainty was estimated by assessing the model sensitivity to varying three input parameters (Guo *et al.*, 2020). In contrast to the parameterized, process-based, and semi-empirical models, the 95% confidence interval could be calculated for the data in the meta-analysis by Stehfest & Bouwman (2006), who reported a mean of 1.8 (0.36 – 7.3) Tg NO-N yr⁻¹ for agricultural fields (cropland and fertilized grassland). Hudman et al. (2012) calibrated the EF (1.5%) in BDSNP so that the BDSNP model predicted a global estimate of NO emissions matching Stehfest & Bouwman's (2006).

Modeling results are not easily verified and should be supported by independent data. In this report, we focused on studies that supported the results with independent data, and we also considered the uncertainty of the validation, such as the uncertainties related to remotely sensing tropospheric NO₂ density data.

Numerous indications in the literature suggest that the CARB inventory (CEPAM) underestimates oxides of N emissions from soil. First of all, the global models predicted that biogenic NO_x sources contribute between 15% and 33% to total NO_x emissions (Table 1) whereas according to CEPAM in 2020, on average, only 2.3% (summer 3.0%, winter 1.6%) of California's total NO_x emissions were of biogenic origin. According to the NEI 2020, biogenic NO_x: total NO_x in California was

7.7%. The biogenic NO_x emissions listed in CEPAM are based on DNDC modeling (Guo *et al.*, 2020), and for NEI, they were based on the Weather Research and Forecasting coupled with Chemistry version 3.8 (WRF-Chem v.3.8) and Biogenic Emission Inventory System version 4 (BEIS4) models.

Second, observations by satellite-mounted instruments and data collected by aircraft during flights in the troposphere support soil NO_x emissions estimates higher than those listed in CEPAM. The data collected by satellite and aircraft are indirect measures as the other NOx sources contributing to NO₂ concentrations in the troposphere (in California, mainly fuel combustion and biomass burning) must be accurate to reliably estimate soil NO_x emissions. Oikawa et al. (2015) reported OMI observations of NO₂ tropospheric column densities in Imperial Valley higher than NO₂ concentrations that included default soil NO_x emission values, or the 10-times higher NO_x emissions measured in local experiments and modeled with MEGANv.2. In another study, Sha et al. (2021) modeled 9-times higher soil NO_x emissions than those listed in CEPAM, but remote sensing by TROPOMI showed that tropospheric NO₂ density that included the default soil NO_x emissions or those modeled (MEGANv.2.04) with BDISNP were both within the uncertainty range of TROPOMI observations. The data collected by aircraft in the SJV also had large errors. Zhu et al. (2023) reported wide ranges of estimated soil NO_x fluxes. However, the lower bounds of those fluxes (1.4 g NO_x-N ha⁻¹ h⁻¹) were higher than the range of soil emissions modeled with MEGANV.2.04 or BEIS (0.15 g NO_x-N ha⁻¹ h⁻¹) thus supporting higher soil NO_x emissions than those listed in CEPAM. Trousdell et al. (2019), also using aircraft for data collection, calculated the lower bounds of biogenic NO_x emission estimates for Fresno, Kings, and Tulare counties as 79 Mg NO_x d⁻¹, corresponding to an average NO_x flux of approximately 1.35 g NO_x-N ha⁻¹ h⁻¹, but the biogenic NO_x emissions listed in the CEPAM inventory were much lower for these three counties (5.6 Mg NO_x d⁻¹). Some doubts about the estimate of total NO_x emissions (216 \pm 33 Mg NO₂ d⁻¹) remain, as the researchers considered the standard error of the mean of six flights as uncertainty rather than the larger errors associated with the conditions and measurement methods during the flights.

Third, Chen et al. (2020), during the DISCOVER-AQ campaign in 2013, noted the underprediction of soil NO_x sources by CMAQv.5.0.2 compared to Pandora measurements at two rural sites (Shafter, Tranquility), which were more than 40% higher than the modeled densities.

Fourth, Lieb et al. (2024) reported higher soil NO_x emissions than in the CEPAM inventory based on N isotope analysis of monthly air samples taken at two locations in the Salton Sea Air Basin. The biogenic NO_x emissions, according to CEPAM, were 0.9 tons $NO_x d^{-1}$ in Calipatria (Imperial County) and 0.1 tons NO_x/d in Thermal, but according to Lieb et al. (2024) they were on average 6.7 (±3.6 and 4.7 (±3.4) tons NO_x/d , respectively.

In contrast to the above studies, which all involved some modeling and/or indirect calculations of soil NO_x emissions, two studies directly measured soil NO_x emissions in California cropland by the soil cover method (Matson *et al.*, 1997; Burger and Horwath, 2013). More than 4000 measurements were made in 15 different cropping systems, most of them at multiple sites with variations in irrigation and fertility management. Fluxes at individual sites ranged from slightly negative to 41.5 g NO_x-N ha⁻¹ h⁻¹, and mean hourly fluxes ranged from 0.02 - 1.35 g NO_x-N ha⁻¹ h⁻¹. The flux chamber measurements did not necessarily indicate higher emissions than shown in the CEPAM inventory, but because measurements were temporally sparse, estimates of cumulative emissions during a whole growing season or year could not be made. Both studies noted inorganic

N availability and proximity to N fertilizer application periods, WFPS, and soil temperature as the most important variables determining the observed fluxes. Burger & Horwath (2013) observed peak NO fluxes coinciding with high soil ammonium concentrations, as well as declines from peak levels once soil ammonium concentrations decreased due to nitrification and crop N uptake. In agricultural soils, applied ammonium is usually quickly nitrified (days to weeks) to nitrate (Robertson, 1997). Decreasing NO fluxes with increasing time since fertilization has been observed in many studies (Williams et al., 1992b; Oikawa et al., 2015). Matson & Firestone (1997) identified a WFPS of about 45% as soil moisture content most conducive to NO flux, whereas NO emissions were rapidly declining at higher soil moisture and more slowly so with declining soil moisture <45% WFPS. Burger & Horwath (2013), on the other hand, in one instance, observed the highest NO flux (41.5 \pm 12.5 g NO-N ha⁻¹ h⁻¹) when the WFPS of the bulk soil was 90% but likely lower at the very surface, where ammonium-containing manure water had been applied. Interestingly, ammonium-nitrate formulations resulted in higher emissions than purely ammoniacal fertilizers (Matson et al., 1997; Liu et al., 2017). Lower NO emissions were observed with subsurface drip and drip irrigation compared to those with furrow-irrigation in the same cropping systems (Hall et al., 1996; Matson et al., 1997; Burger and Horwath, 2013).

Whereas the number and frequency of measurements in the above two surveys of NO_x fluxes were not adequate to allow calculation of seasonal emissions, Matson et al. (1998) performed enough flux measurements to estimate NO and N₂O emissions in two subsequent crop cycles of irrigated wheat in the Yaqui Valley, Mexico based on daily to weekly sampling. The researchers measured 4.3 and 8.9 kg NO-N ha⁻¹ and 2.2 and 2.4 kg N₂O-N ha⁻¹ during the 1994/95 and 1995/96 wheat growing seasons, respectively, in a system fertilized according to farmers' practice with 250 kg N (187 kg urea-N ha⁻¹ applied one month before planting and 63 kg N anhydrous ammonia ha⁻¹ applied as side-dress) (Matson *et al.*, 1998; Panek *et al.*, 2000; Ahrens *et al.*, 2008). Based on the frequent measurements, seasonal emissions could be calculated, and alternative fertilization regimes were evaluated in additional experiments. In an alternative practice, only 180 kg N was applied, one-third at planting and two-thirds as side-dress, and this resulted in emissions of NO and N₂O together of only 0.74 kg N ha⁻¹ (Matson *et al.*, 1998).

The above two studies in California focused on agricultural soil during summer. There is little doubt that agricultural soils, fertilized with mostly ammoniacal synthetic N and manures, during summer are the major source of soil NO_x emissions in temperate latitudes (Williams *et al.*, 1992a; Williams *et al.*, 1992b; Butterbach-Bahl *et al.*, 2009). The summer growing seasons have been the time when most NO flux measurements have been conducted in temperate climate zones, but Martin et al. (1998) reported that 25% of annual NO_x emissions (0.8-1.8 kg NO-N ha⁻¹ yr⁻¹) in a short-grass steppe in Colorado occurred during winter. In California, soil NO flux has not been measured throughout the year.

Substantial NO_x emissions may also occur after fires. In soil of burned chaparral, 3 kg NO-N ha⁻¹ was lost during six months, compared to only 1 kg NO-N ha⁻¹ during the same period in unburned soil of the same ecosystem, indicating that much of the ammonium produced by the burning of aboveground vegetation is lost as NO (Anderson and Poth, 1989).

6. Recommendations

The fact that soil NO_x emission data in California are temporally sparse has made estimation and modeling of soil NO_x fraught with uncertainties. Our criteria for evaluating California N gas emissions studies and modeling were that results had to be supported by independent data and statistics. In this report, we also considered the uncertainty of model validation data, such as the uncertainties of remotely sensed tropospheric NO_2 density data.

Some of the above-mentioned studies suggest that the current CEPAM inventory of oxides of N may be too low (Oikawa *et al.*, 2015; Trousdell *et al.*, 2019; Chen *et al.*, 2020; Zhu *et al.*, 2023; Lieb *et al.*, 2024). It is also noteworthy that CEPAM's NO_x inventory value for California was lower than any other estimates of California's NO_x emissions (Table 1). Currently, DNDC modeling results inform CEPAM. The configuration of the DNDC model was comprehensive and covered most major land-use types with soil NO_x emission potential, but the field data used to validate the modeling results were temporally too sparse to allow for computing seasonal emissions in the different cropping systems. It is therefore recommended that CARB obtain additional NO_x emissions data (more details below).



Figure 16. Flowchart showing how additional data sources will feed into a process-based model which can then inform CARB's soil NO_x inventory. Black arrows represent data inputs to the model or data that are needed to calculate NO_x flux by other methods; blue solid lines represent model outputs; blue dashed lines represent NO_x emission data of methods that also require input of NO_x sources other than soils; dashed red arrows represent NO_2 density data that must be converted to NO_x emission data by modeling.

Figure 16 shows how additional data can be used to make CARB's soil NO_x inventory more robust. To cope with the temporal and spatial variability of NO_x emissions and the uncertainty of modeling results, future assessments of NO_x emissions must take advantage of the various measurement approaches in concert. For example, incorporation of accurate spatial and temporal patterns of N fertilization, NO_x flux measurements, monitoring of NO_x concentrations at ground level, and remotely sensed column densities of NO₂ would ideally be performed for the same area and time period in order to calibrate models and validate NO_x modeling results with independent data. The numbers in parentheses within the flowchart figure refer to the details of each data stream described below.

There is a need for continuous measurement of NO_x flux in cropland, or at a minimum, for frequent NO flux measurements (daily to weekly) throughout the year (5). Such measurements are suggested in forage production systems receiving manure in liquid and solid form, furrow-irrigated field crops, as well as sprinkler- or surface drip-irrigated orchard crops. Soil NO fluxes observed by the soil cover method represent direct measurements of NO escaping from soil. Such measurements would show the NO_x emission dynamics in response to N fertilization and different irrigation methods during the entire cropping season and post-harvest, fallow, rotation crop, and field preparation seasons. Having datasets of NO_x flux throughout an entire year will make it possible to better calibrate and validate process-based and partially mechanistic models of NO_x emissions (6). Soil fluxes of NO can be measured with static and dynamic chambers and a chemiluminescence analyzer. The chambers must be placed at replicated locations representative of the different soil moisture dynamics in a field. For example, in furrow-irrigated fields, soil moisture and compaction levels are typically very different in the furrow, the shoulder of a bed, and the center of the bed. In addition to soil moisture, the location of the N fertilizer placement must also be considered. The limitation of flux chamber methods is the small area of soil surface that each chamber covers. This limitation must be mitigated as best as possible through careful chamber location selection and replication. It is also possible to measure NO continuously using newly available laser instrumentation or a flux gradient or eddy covariance method (Taylor et al., 1999; Min et al., 2014) (3). The advantages of these methods are the ability to capture hot moments of emissions; towers yield greater spatial representation (e.g., one ha according to Min et al., 2014) than flux chamber methods, and the ability to measure above-canopy NO_x flux emissions. However, tower-based approaches make it more difficult to partition sources, as mentioned above.

To cope with the uncertainty of modeling results and to be able to continuously monitor ambient NO_2 mixing ratios as an integrated measure of the effects of soil NO_x emissions and other potential NO_x sources, additional ambient air quality monitoring sites in rural locations, preferably surrounded by agricultural fields, would be very useful for CARB and regional air quality monitoring (4). Almost all current ground-based air pollutant monitoring stations are in urban and near-highway locations. Adding additional instrumented sites capable of continuously monitoring ambient NO_2 and O_3 concentrations in rural locations could provide direct information on the effects of soil NO_x emissions if the inventory of the other ambient NO_x sources is accurate. Ideally, flux chambers will be employed near sites of continuous ambient NO_2 monitoring instruments.

As mentioned above, estimating soil NO_x emissions based on total NO_2 in the troposphere (e.g., by remote sensing or ground-based monitoring instrument) requires accurate estimates of NO_x from sources other than soil (1). This includes mobile and stationary sources such as on-road and off-road diesel engines, wildfires, biomass burning among others. Other methods, such as NO_2 data collected by aircraft (2), or eddy covariance flux tower data (3), also require knowledge of the magnitude of other NO_x sources. The NO_2 column densities observed with OMI, TROPOMI, and TEMPO (NASA geostationary satellite, in operation since 2023, providing <u>hourly</u> data with a spatial resolution of 2 km × 4.75 km) can be used for validation of bottom-up estimates if reliable estimates of all sources are available, but also to locate areas with high high-density NO_2 columns, e.g. in agricultural regions. With increasing spatial and temporal resolution of remotely sensed data, tracking air pollutants over time, e.g., after N fertilizer applications (7), could yield useful information about NO_x sources.

Field research in China showed that ammoniacal fertilizer is a strong HONO source (Xue et al., 2021), and modeling indicated that HONO increases O_3 levels (Zhang et al. 2016, 2017; Xue et al. 2021). Few field measurements of HONO emissions have been made in California, and relatively little is known about the magnitude and relevance of HONO emissions from soil to California air quality (Ren *et al.*, 2011; VandenBoer *et al.*, 2014). Incorporation of HONO data, including HONO emissions from soil, could potentially improve tropospheric air quality modeling (8).

A regularly updated database of N fertilizer uses and times of application could be most useful for modeling. The California Water Boards, on behalf of the Irrigated Lands Regulatory Program, collect information on N fertilizer applications and irrigation types by crop for different regions, and information on the timing of the applications may be obtained from UC Cooperative Extension Specialists and county Agricultural Commissioners. Having accurate information about N fertilizer applications, especially the timing of applications, will improve the parameterization of NO_x models as the time of fertilizer applications is a critical variable for predicting NO_x flux (9).

In irrigated agriculture, soil moisture is a dynamic variable. The approach of Deng et al. (2018a) in estimating soil moisture status for DNDC modeling of N_2O emissions is a reasonable approximation to model soil moisture in irrigated crop fields. The approach entailed using the amount of water applied with different irrigation methods and an applicable irrigation efficiency factor for a given crop, based on California Department of Water Resources (CDWR) survey data, and dividing the total water application by the number of irrigations per growing season (10). Information on the acreage of a given crop irrigated by each method was from Cost and Return studies for crop commodities in California by UC Davis. Some parameters, such as the frequency of surface gravity irrigation and the depth of the drip tape reported in Deng et al. (2018a), must be updated. The DNDC model computed WFPS based on water inputs and soil properties.

Pulsing, the rapid NO emission response to rewetting after soils have been dry for extended periods has been estimated to contribute between 3-24% to soil annual NO_x emissions (Davidson *et al.*, 1991b; Yienger and Levy, 1995; Steinkamp and Lawrence, 2011). Depending on environmental/meteorologic circumstances, a significant part of a site's total soil NO_x annual emissions may be released within 1-2 days after rewetting, but the importance of pulsing in California's agricultural land has not been demonstrated. In California's cropland, potentially large NO emissions could occur with the first wet-up (rain) in the fall after fields have been dry and accumulating NO₂⁻ and mineralizable organic substrate near the soil surface (Slessarev *et al.*, 2021) for an extended time after the summer irrigation season. The soil near the surface of subsurface drip-irrigated fields remains mostly dry all summer. Information about pulsing could improve inventory numbers and modeling (5).

Similar challenges exist for NH₃ and N₂O measurements. For NH₃, new approaches and instrumentation for continuous measurements are becoming available to improve flux estimations (Wang *et al.*, 2021; Pedersen et al., 2023), particularly for focusing on soils amended with manure

and digestate, as well as subsurface drip irrigation and the use of nitrification inhibitors. Continuous soil pH monitoring would facilitate the modeling of NH₃ emissions (Crichton *et al.*, 2025). Instrumentation for continuous measurement of N₂O fluxes is becoming widely available, along with sensors for continuous measurement of oxygen, moisture, and temperature, important drivers of N₂O emissions (Anthony and Silver, 2021). The periodic nature of nitrogenous gas fluxes requires continuous measurement to capture hot moments of emissions and better quantify annual inventories. More studies focusing on organic and inorganic N-rich amendments are needed, as well as to investigate the impacts of micro-irrigation and fertigation practices on gaseous N losses.

7. References

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