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Agriculture is a major source of NO_x pollution in California

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Nitrogen oxides (NO_x = NO + NO₂) are a primary component of air pollution—a leading cause of premature death in humans and biodiversity declines worldwide. Although regulatory policies in California have successfully limited transportation sources of NO_x pollution, several of the United States' worst-air quality districts remain in rural regions of the state. Site-based findings suggest that NO_x emissions from California's agricultural soils could contribute to air quality issues; however, a statewide estimate is hitherto lacking. We show that agricultural soils are a dominant source of NO_x pollution in California, with especially high soil NO_x emissions from the state's Central Valley region. We base our conclusion on two independent approaches: (i) a bottom-up spatial model of soil NO_x emissions and (ii) top-down airborne observations of atmospheric NO_x concentrations over the San Joaquin Valley. These approaches point to a large, overlooked NO_x source from cropland soil, which is estimated to increase the NO_x budget by 20 to 51%. These estimates are consistent with previous studies of point-scale measurements of NO_x emissions from the soil. Our results highlight opportunities to limit NO_x emissions from agriculture by investing in management practices that will bring co-benefits to the economy, ecosystems, and human health in rural areas of California.

INTRODUCTION

Nitrogen oxide (NO_x = NO + NO₂) gases are among the most important components of air pollution, which, according to the World Health Organization, is responsible for one in eight premature deaths worldwide (1). These nitrogen (N) gases have been linked to upper respiratory disease, asthma, cancer, birth defects, cardiovascular disease, and sudden infant death syndrome (2, 3). Global studies have pointed to similarities in the magnitude of NO_x emissions from fossil fuel combustion and soil, with the largest soil emissions from regions with heavy N fertilizer applications (4–7). Despite the significance of soil microbial NO_x emissions at the global scale, policies have focused largely on limiting NO_x from mobile and stationary fossil fuel sources (8, 9). Where agriculture is an important source of NO_x, strategies to reduce nonpoint emissions will need to incorporate soil management approaches and policies that are fundamentally different from fossil fuel sources.

California is considered the world's sixth largest economy in terms of gross national product and supports 12.2% of the U.S. food economy (10). The state has instituted policies to reduce NO_x pollution from fossil fuel sources, resulting in NO_x declining by 9% per year in Los Angeles, San Francisco, and Sacramento over the period of 2005 to 2008 (11). Recent findings have suggested that agriculture is one of the dominant sources of NO_x in the United States, particularly in the midwest region, where fertilizer inputs are substantial (6, 12). In California, local field measurements have similarly ascribed high NO_x emissions to agricultural soil (13). Matson *et al.* (14) provided some of the first evidence of substantial NO_x production from agricultural soils in California's Central Valley; however, a statewide assessment, which is needed to drive new policies for NO_x pollution, is hitherto lacking. The California Air Resources Board

(CARB) estimates that ~3.8% of the state's NO_x budget can be attributed to cropland soils, but these estimates are based on data limited to farms located within 200 km of Sacramento and miss many of the most heavily fertilized areas in the state (15). Moreover, CARB does not include these estimated emissions in their official statewide database for air quality modeling (16).

Here, we provide the first large-scale quantification of soil NO_x emissions for California through two different approaches: integrative “bottom-up” spatial modeling and “top-down” airborne NO_x measurements. This two-pronged approach allows us to independently examine the contribution of biogenic NO_x emissions in California while comparing these estimates to local empirical data. Our overarching hypothesis is that biogenic emissions of NO_x from agricultural areas are much higher than we used to believe and could be a major source of atmospheric NO_x statewide. Alternatively, if agricultural sources are of minor significance, then we would expect to find uniformly low emissions throughout natural and agricultural ecosystems.

RESULTS AND DISCUSSION

Our combined bottom-up and top-down estimates uniformly point to high NO_x emissions from California's agricultural soil, revealing a significant unrecognized source of N pollution statewide. Our bottom-up model reveals that 161,100 metric tons of NO_x-N year⁻¹ is emitted from California soil with croplands accounting for 79% of total emissions. When combined with data on existing mobile and stationary fossil fuel sources (16), our results indicate that fertilized croplands account for 20 to 32% of total NO_x-N emissions from all sectors of the state, whereas natural soils account for 5 to 9% (Fig. 1). A meta-analysis of soil NO_x emissions from the existing literature demonstrates quantitative coherence between our model-based estimates and empirical measurements from different areas of the state (Table 1). Mean NO_x emissions from California cropland soils were 19.8 (±27.3 SD) kg of N ha⁻¹ year⁻¹ and ranged from 0 to 276 kg of N ha⁻¹ year⁻¹ (Fig. 2), with 1/4 quartile and 3/4 quartile values of 4.3 and 24.9 kg of N ha⁻¹ year⁻¹, respectively. NO_x emissions were largest from agricultural soils where N fertilizer applications can reach >600 kg of N ha⁻¹ year⁻¹ (average N fertilizer

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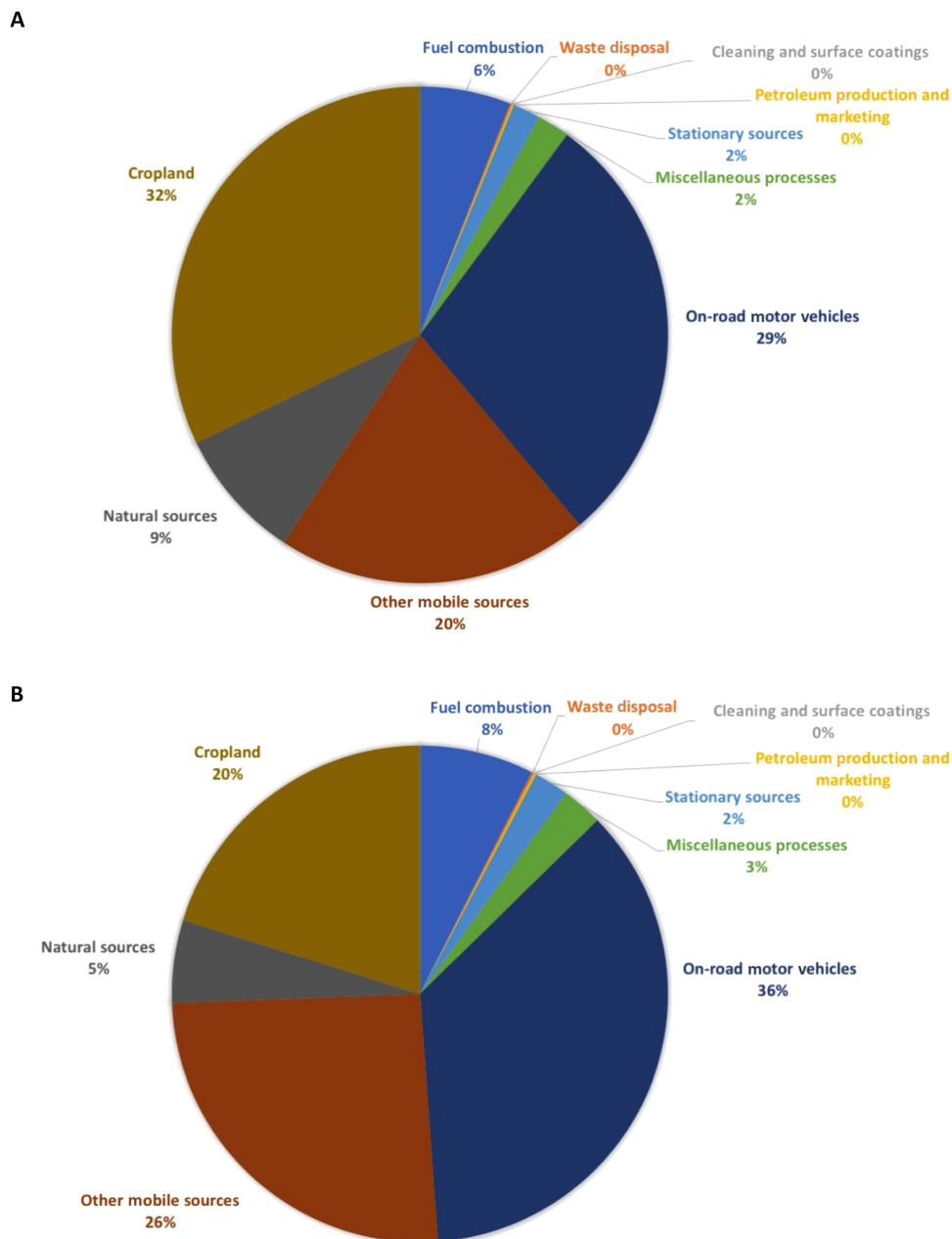


Fig. 1. Contribution of soils to statewide NO_x emissions. Based on CARB emission estimates and IMAGE-modeled emission estimates for cropland and natural ecosystems (A) without vegetation scavenging (gross rates) and (B) with 50% of NO_x emissions scavenged by vegetation (net rates).

rates for fertilized soils, 131.8 kg of N ha⁻¹ year⁻¹; Fig. 3). A spatial maximum hot spot of soil NO_x emissions is identified for southern reaches of the state, where climate is relatively hot and arid (17). The model also predicts local maxima in the Sacramento Delta region, the Salinas Valley, and the San Joaquin Valley, with the latter being confirmed by aircraft measurements (see below).

Modeled NO_x emissions track N fertilizer applications

Our findings support the hypothesis that biogenic sources represent a significant fraction of NO_x emissions in California, particularly in areas with high N fertilizer applications. Although we report gross soil emission estimates, NO_x uptake by vegetation can cut atmo-

spheric NO_x emissions in half (4, 18). We thereby provide a more conservative estimate that attributes 25% of statewide NO_x to the soil (Fig. 1B), which assumes that half of the soil NO_x is lost to dry deposition within nearby vegetation canopies. Reducing uncertainty regarding the soil contribution of NO_x to the statewide budget will require spatial and temporal assessments that can distinguish between sources.

Our findings for California are consistent with previous global-scale estimates given the tremendous agricultural productivity of the state: Yienger and Levy (4) used a model to demonstrate that soils account for 50% of the total NO_x budget in remote agricultural regions of the Northern Hemisphere, Jaeglé *et al.* (6) found that soils were

Table 1. Modeled values and observed values collected from the literature of NO emissions in California. LAT, latitude; LONG, longitude; SFREC, Sierra Foothill Research and Extension Center.

Site	LAT	LONG	Modeled NO (kg of N ha ⁻¹ year ⁻¹)	Observed NO (kg of N ha ⁻¹ year ⁻¹)	Observed NO range (kg of N ha ⁻¹ year ⁻¹)	Reference
Imperial Valley	32.8476	-115.5694	20.6	21.0	0–280	(13)
SFREC	39.2513	-121.3137	2.5	3.5	4–31	(27)
Barton Flats	34.2439	-116.9114	1.1	1.0	0–2	(28)
Camp Paivika	34.2429	-117.2683	3.7	5.0	3–7	(28)
Stanford	37.4241	-122.1661	1.9	3.5	0–7	(29)
San Dimas	34.1797	-117.7681	0.0	3.0	0–19	(30)
Bonadelle Ranchos	36.9693	-119.8873	4.5	7.1	4–12	(14)
Clovis	36.8252	-119.7029	1.6	0.9	0–3	(14)
Corcoran	36.098	-119.5604	0.2	0.1	—	(14)
Firebaugh	36.8588	-120.456	27.7	6.7	1–18	(14)
Kearny	36.6008	-119.5109	17.3	2.8	0–21	(14)
Lindcove	36.3578	-119.0636	19.6	1.3	1–2	(14)
Mendota	36.7536	-120.3816	23.9	0.7	0–1	(14)
Parlier	36.6116	-119.5271	2.9	5.6	0–22	(14)
Plainview	36.144	-119.1326	38.1	13.7	0–46	(14)
Riverdale	36.4311	-119.8596	28.3	0.1	0–1	(14)
San Joaquin	36.6066	-120.189	5.5	7.2	1–57	(14)
Sanger	36.708	-119.556	9.1	9.6	—	(14)
Tranquility	36.6488	-120.2527	52.9	2.1	2–3	(14)
Tulare	36.2077	-119.3473	20.6	0.1	0–1	(14)
Waukena	36.1382	-119.5099	10.4	0.4	0–1	(14)

responsible for 22% of worldwide NO_x emissions, Wang *et al.* (7) estimated that agricultural soils were responsible for 20 to 30% of global NO_x sources, and Davidson *et al.* (5) estimated that soils were responsible for 10% of emissions in the Southeastern United States, with agriculture contributing to 75% of total soil NO_x emissions. Furthermore, our soil NO_x emission estimates are on par with those from agrarian areas in Europe (24 to 62%) (19) and during the crop-growing season in the midwestern United States (15 to 40% in June and July) (12).

In contrast to high mean efflux from agricultural soils (average, 19.8 kg of N ha⁻¹ year⁻¹), NO_x emissions from natural ecosystems were much lower (average, 1.0 kg of N ha⁻¹ year⁻¹). This points to the importance of N inputs (in fertilizer) in accelerating NO_x emissions from soil microbial communities (20). Our model-based estimates compared favorably with published literature values for California and beyond, which range from 0 to 25 kg of N ha⁻¹ year⁻¹ (Table 1). Likewise, in the southern and midwestern regions of the United States, empirically measured NO_x emissions from cultivated soils are on the order of 3 to 14 kg of N ha⁻¹ year⁻¹ versus 0.1 to 3 kg of N ha⁻¹ year⁻¹ from nearby unfertilized grasslands (21–25). Other studies have also demonstrated

that cultivated land produces NO_x emissions an order of magnitude larger than forest soils in the same biome (26).

Emission estimate variability

Modeled soil NO_x emissions produced ranges that were similar to those reported in the literature (Table 1). Both modeled and observed (in situ chamber measurements) emissions were typically less than 5 kg of N ha⁻¹ year⁻¹, with larger values in the Imperial Valley (located in Southern California between the Salton Sea and Mexico; Fig. 2). Whereas most observed values were similar to those of the model, NO_x emissions showed marked variability, consistent with spatial heterogeneities of soil microbial processes. Biogenic NO_x emissions can also vary temporally, with the largest emissions spiking when fertilizers are applied (12). The timing of fertilization in California varies regionally, considering the variety of crop species grown and the different management practices used. Our model validation was restricted to a handful of empirical studies (13, 14, 27–30), which demonstrate the need for more ground measurements throughout California to better assess the local impact and spatial distribution of soil NO_x emissions.

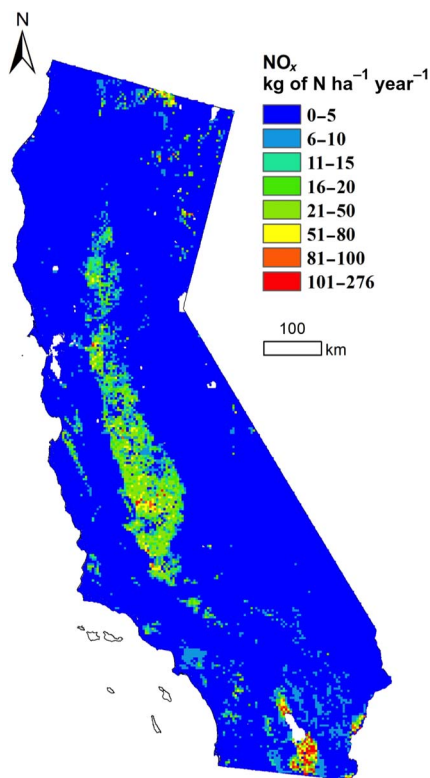


Fig. 2. Estimates of NO_x emissions from California soils (natural and cropland) generated by using stable isotopic modeling and IMAGE model.

Surface emissions estimates from airborne NO_x observations

We used airborne measurements of NO_x concentrations to estimate regional emissions in the San Joaquin Valley. This allows us to further verify our model and determine how NO_x emissions from the soil might affect regional compliance with ambient air quality standards, which are based on 1-hour and annual average concentration thresholds (31). Our top-down approach involved repeated airborne measurements of NO_x made between Fresno and Visalia during the summer of 2016 (fig. S3) in conjunction with the California Baseline Ozone Transport Study (CABOTS) coordinated by CARB. Careful accounting of the height of the atmospheric boundary, coupled with direct measurements and some judicious estimates of all the terms in the NO_x concentration budget equation, allowed us to estimate surface emissions (32) of NO_x in the region of the flight experiment (see the Supplementary Materials). The average of six flight days (three at the end of July and three at the beginning of August) over a region of ~720,000 ha yielded a NO_x emission estimate of 190 ± 130 metric tons day⁻¹. According to the CARB California Emissions Projection Analysis Model (CEPAM) (33), which includes fossil fuel but not natural sources, the sum of average summertime NO_x emissions over all three counties in the surrounding area (Fresno, Tulare, and Kings covering over 3.1 million ha) amounts to 100 metric tons day⁻¹. Although the exact area and diurnal timing of the emissions from the CEPAM inventory cannot be precisely compared to the spatial and temporal footprint of our airborne sampling, the comparison between the CEPAM inventory and airborne sampling shows that soil emissions are likely a very important source of atmospheric NO_x, especially in the agriculturally intensive San Joaquin Valley. In this case, the agricultural soil source would need to account for at least

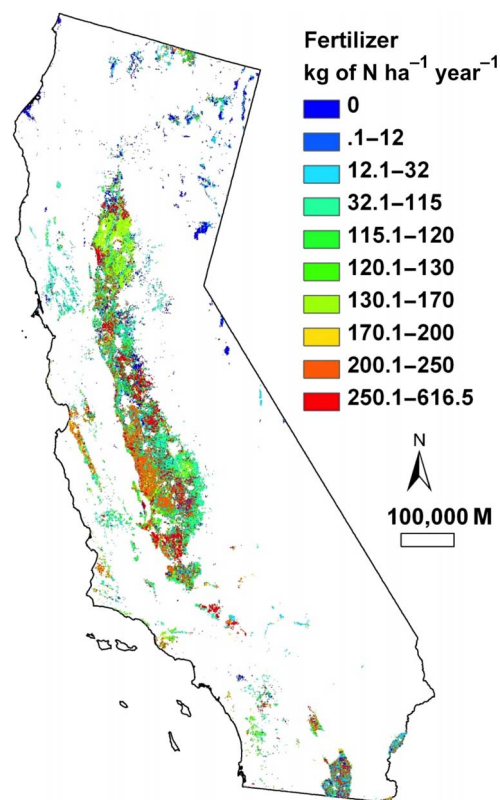


Fig. 3. Nitrogen fertilizer inputs to California soils. Fertilizer application rates are generated based on crop type, using crop-specific data provided by the DWR of California and USDA fertilizer consumption database for 1964 to 2006.

47% of the total NO_x emissions or a regional flux of $12.4 \text{ kg of N ha}^{-1} \text{ year}^{-1}$ (table S4). We consider this to be a conservative estimate because the county inventories make up a much larger area than the flight domain. Furthermore, the flights did not span either commuter rush hour, when NO_x emissions are at their daily peak. We conclude that soils most likely contribute a majority of all NO_x emissions to the atmosphere in the agriculturally intensive central San Joaquin Valley.

Comparing emissions estimates between methods

We compared surface emissions estimates for the San Joaquin Valley with soil model estimates for the same region (fig. S3 and table S4). Using year-round mean emissions for both natural and cropland soils, our model generated an annual flux of $24 \text{ kg of N ha}^{-1} \text{ year}^{-1}$ for the central San Joaquin Valley, between Fresno and Visalia, and as high as $36 \text{ kg of N ha}^{-1} \text{ year}^{-1}$ during the season of the airborne measurements (July to August), which yielded fluxes ranging from 14 to $39 \text{ kg of N ha}^{-1} \text{ year}^{-1}$. The correspondence between the bottom-up and top-down estimates builds robustness into our estimates for statewide NO_x emissions and confirms our working conclusion for substantial NO_x emissions from fertilized croplands in the Central Valley.

Our soil model estimates are slightly higher than, although comparable with, the few number of empirical measurements of NO_x emissions from the San Joaquin Valley's cropland soils (made between July and September of 1995) (14), which ranged from 0.1 to $14 \text{ kg of N ha}^{-1} \text{ year}^{-1}$ (Table 1). That we estimate higher soil NO_x fluxes via the top-down and bottom-up approaches is consistent with more recent empirical measurements (13), suggesting that increases in N fertilizer

use and population growth have likely accelerated soil NO_x emissions since the last time empirical measurements were reported for the region, some 20 years ago (14).

Controls on soil NO_x emissions

Previous studies have demonstrated that NO_x emissions are controlled by water-filled pore space (influenced by precipitation, irrigation, and soil texture) (34), N availability (20), and temperature (13), all of which were fundamental parameters in our model-based estimate of soil NO_x emissions in California (that is, the model relies on functions related to soil organic carbon, soil texture, drainage, temperature, and precipitation). We performed a model sensitivity analysis by evaluating the response of cropland denitrification rates to model input parameters at the ±10% level and examined the effect size of this parameter variation on NO_x emissions. We found that soil NO_x emissions were least sensitive to changes in soil carbon and were much more responsive to changes in soil texture, soil drainage, and climate (fig. S2).

Nitrogen input rates and climate were primary determinants of soil NO_x emissions in our model. The largest chamber-based measurements of soil NO_x emissions come from the Imperial Valley in Southern California (Table 1) (12), which was accurately predicted by our model, implying that our model is capable of detecting hot spot emissions. High emissions in the Imperial Valley are likely explained by three factors. First, a biogenic source in these soils suggests a kinetic response to high temperatures that occur in this region. Second, arid soils not only produce more NO_x relative to N₂O and N₂ but also allow for the build-up of inorganic N via nitrification; N that will then be released in large quantities when soils are irrigated and microbial denitrification is triggered. Third, high fertilizer inputs that increase N availability in the soil may help soils to develop a healthy community of nitrifying bacteria, providing a positive feedback to N availability and subsequent loss.

Implications for California

The CARB emission inventory provides an assessment of air pollution magnitudes and sources in California. Sources are inventoried based on four main categories: mobile, stationary, area-wide, and natural. In the current CARB NO_x inventory, mobile emissions are thought to predominate (83%), whereas soil emissions are currently considered negligible (16). Here, we show that agricultural soils contribute a substantial amount of NO_x to the atmosphere. We can expect to see the significance of biogenic NO_x emissions increase as N fertilizer inputs increase to keep pace with food demands (35) and automotive NO_x controls continue to attenuate mobile fossil fuel sources. Our findings suggest the need to reconsider the role of soil NO_x sources and provide a pathway to constrain these diffuse pathways into CARB inventory analyses. Recent climate changes in California have caused pronounced heat waves and drought, factors which could exacerbate biogenic NO_x emissions, leading to increased air pollution and N deposition rates in natural ecosystems (8). Considering the limited number of field-based NO_x measurements and the difficulty involved with partitioning soil versus fossil fuel sources through satellite imagery, a more robust field sampling strategy of soil NO_x emissions throughout the state could aid in efforts to understand agricultural impacts on air pollution in the Central Valley.

Several existing approaches could be used to reduce soil NO_x emissions from fertilized croplands. There are many strategies to improve fertilizer efficiencies, which would minimize the unwanted risks of N fertilizer spillovers into the environment and benefit farmers

by reducing fertilizer costs. Where mineral fertilizers are used exclusively, for example, applying different forms of fertilizer (for example, slow-release fertilizers) (36) or lowering N applications and using precision agriculture to target developmental stages (37), have been shown to cut N fertilizer losses from cropland soil. Where organic amendments are applied, separating the application timing of mineral N and organic fertilizer has been shown to reduce N emissions (38). Precision fertilization, as opposed to broadcasting, can also increase N uptake and minimize losses (39). Cover crops that consume residual N, which can subsequently be incorporated into the soil, are another option for reducing N fertilizer application rates (40). A complementary institutional strategy would be to incentivize plant production for human versus livestock consumption because livestock manure and the N used to grow livestock feed are major sources of N pollution in the air and water (3). Another strategy would be to promote the reduction of NO_x to an environmentally benign gas such as dinitrogen (N₂), which can be achieved by installing riparian zones to collect fertilizer runoff or introducing nitrification inhibitors to stem denitrification rates (3, 41). The ratio in which harmful (NO_x and N₂O) and inert (N₂) gases are emitted from soils depends heavily on N availability, soil moisture, and temperature; thus, irrigation strategies are another important step to reduce N losses from agriculture.

These and many other strategies can help to reduce potentially harmful N losses from agriculture (3, 42, 43). Losses of N fertilizer are not only costly to farmers but can also create economic costs to the greater United States on the order of \$210 billion dollars per year in health and environmental damages (43, 44). Reducing NO_x emissions therefore offers a win-win situation for farmers, environmental health, and the economy.

CONCLUSIONS

This study builds on local point-scale measurements (14) to provide the first spatially explicit evidence of substantial NO_x emissions from agricultural soils in California, a previously unrecognized source that is estimated to contribute 20 to 51% of the state's total NO_x budget. These soil NO_x emissions are sourced to N fertilizer applications in Central Valley croplands. The effect of large soil NO_x emissions on air quality and human health remain unclear, but the magnitude of the flux alone raises concern about its potential impact, particularly in rural California. Where biogenic sources affect air quality and health, the implementation of strategies to reduce these emissions will be imperative. A better understanding of the sources, distribution, and impact of biogenically produced NO_x will improve our ability to mitigate emissions in the future.

MATERIALS AND METHODS

To model the spatial distribution of soil NO_x emissions, we used an N isotope model (17, 45) in natural areas and an Integrated Model for the Assessment of the Global Environment (IMAGE) (46) in cropland areas to estimate total N losses from soils based on the surplus of N in the environment [see the study of Wang *et al.* (7) for model details]. The N surplus was a function of N inputs (deposition, fixation, fertilizer, and irrigation) minus N outputs besides denitrification and leaching (crop harvest and ammonia volatilization). Manure and grazing were not included as inputs/outputs; instead, we considered them as recycling functions of internal N cycling. Surplus N was then partitioned between leaching and gaseous losses based on temperature, precipitation

(irrigation), evapotranspiration, soil texture, soil drainage, soil organic carbon content, soil total available water content, and land cover (see the Supplementary Materials). Gaseous losses were partitioned between NO, N₂O, and N₂ based on water-filled pore space (fig. S1). The resulting NO flux in California was between 0 and 276 kg of N ha⁻¹ year⁻¹ with one outlier (525.7 kg of N ha⁻¹ year⁻¹) being removed.

All data sets were transformed to 4000-m × 4000-m spatial grids before model runs. We used the California Augmented Multisource Land Cover Map published by the Information Center for the Environment, University of California, Davis (UC Davis). Temperature and precipitation data (mean from 1971 to 2000) were from the PRISM (Parameter-elevation Regressions on Independent Slopes Model) Climate Group, Oregon State University, created on 4 June 2010 (47). Nitrogen deposition data were based on the Community Multiscale Air Quality model by Tonnesen *et al.* (48). Nitrogen fertilizer application rates were from the Department of Water Resources (DWR) of California and U.S. Department of Agriculture (USDA) fertilizer consumption database for 1964 to 2006. Nitrogen harvest was calculated by multiplying crop production by percent dry matter by percent N for each crop type at each year. We then used the mean value for each crop type from 1980 to 2007. The data were from the USDA National Agricultural Statistics Service (2012) and the UC Davis Agricultural and Resource Economics. Nitrogen irrigation data were from the DWR irrigation database for 2001, assuming that N content in irrigation water was 1 mg of N liter⁻¹ water. We used a fixed N fixation rate for different crops: rice, 2.5 kg of N ha⁻¹ year⁻¹; beans, 40 kg of N ha⁻¹ year⁻¹; alfalfa, 400 kg of N ha⁻¹ year⁻¹; clover, 15 kg of N ha⁻¹ year⁻¹; and natural vegetation, 5 kg of N ha⁻¹ year⁻¹ (10). The ammonia volatilization rate was estimated to be 3.6% of N fertilizer, as reported in the California Department of Food and Agriculture Fertilizer Research and Education Program, and to be 15 kg of N ha⁻¹ year⁻¹ in manure applied areas and 1.6 kg of N ha⁻¹ year⁻¹ in urban areas (49). Soil properties data, including soil texture, soil drainage, SOC (soil organic carbon) content, and total available water content, were from the USDA Soil Survey. We collected data from the literature, which we then compared to our model generated fluxes. Data were collected using Google Scholar and some combination of the following search terms: “NO_x,” “nitrogen oxides,” “nitric oxide,” “emissions,” “trace gas,” “California,” and “site name.” References were then followed from papers that were found to be useful.

The airborne NO measurements were made with an Eco Physics (model CLD 88) chemiluminescence instrument with a stabilized photomultiplier tube and reaction chamber temperatures and other operating parameters to ensure a steady calibration point and high reproducibility. A blue-light light-emitting diode photolytic converter (Model 42i BLC2-395 manufactured by Air Quality Design Inc.) was used to selectively convert NO₂ to NO for alternating measurements of NO_x (= NO + NO₂). Further, a Teflon prereaction chamber was installed to run the chemiluminescence reaction to completion before the detection cell to keep track of any interferences or changes in the background signal, thereby increasing the confidence in the measurements and lowering the detection limit generally to less than 0.05 parts per billion by volume. The instrument was cycled through the three states of NO and NO_x and background measurements were done every 20 s. Calibrations were performed by O₃ titration with a National Institute of Standards and Technology traceable NO standard (Scott-Marrin Inc.) certified to within 5%. Full calibrations were performed before and after the entire flight series, with zero and span checks run routinely before and after each flight. The aircraft used to conduct the experiment is operated by Scientific Aviation Inc. (<http://scientificaviation.com/overview/>).

Emission estimates were made using a simple boundary layer budget equation for NO_x (see the Supplementary Materials). This technique was outlined in the study of Lenschow *et al.* (50), can be generalized to any scalar (51–54), and was recently used to estimate regional methane emissions in the San Joaquin Valley (32). The technique involves thoroughly probing the atmospheric boundary layer (ABL) over a particular region via aircraft, horizontally and vertically, to determine the time rate of change, horizontal advection, and vertical mixing for various scalars, as well as the boundary layer height and its growth. This technique permits the calculation of residual terms within the scalar budgets for the region of interest (32). See the Supplementary Materials and Trousdell *et al.* (32) for greater details of the budget method, error estimates, and the other aircraft measurements.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at <http://advances.sciencemag.org/cgi/content/full/4/1/eaao3477/DC1>

Supplementary Methods

table S1. Crop classification and fertilizer rate data (mean for 1964 to 2006) collected from the DWR of California and USDA fertilizer consumption database.

table S2. ABL heights, z_r, and budget terms for the six flights.

table S3. NO_x budget table and the consequent total regional emissions for each flight.

table S4. Flight estimates of total NO_x and soil NO_x and model estimates of soil NO_x for the flight area in fig. S3 [Coordinates box: (36°51'52.09"N, 120°43'19.65"W), (37°0'6.85" N, 119°50'53.87"W), (35°57'49.03"N, 120°1'37.93"W), and (36°5'27.03"N, 118°58'2.91"W) compared with CARB inventory of total NO_x].

fig. S1. Model of how nitrogen oxide (NO), nitrous oxide (N₂O), and dinitrogen (N₂) partitioning varies with water-filled pore space.

fig. S2. Sensitivity of NO emission from croplands to different input parameters: soil organic carbon (f_{soc}), soil texture (f_{txt}), soil drainage (f_{drain}), and climate (f_{clim}).

fig. S3. Airborne NO_x observation sampling area.

References (55–58)

REFERENCES AND NOTES

- World Health Organization (2014); www.who.int/mediacentre/news/releases/2014/air-pollution/en/.
- A. R. Townsend, R. W. Howarth, F. A. Bazzaz, M. S. Booth, C. C. Cleveland, S. K. Collinge, A. P. Dobson, P. R. Epstein, E. A. Holland, D. R. Keeney, M. A. Mallin, C. A. Rogers, P. Wayne, A. H. Wolfe, Human health effects of a changing global nitrogen cycle. *Front. Ecol. Environ.* **1**, 240–246 (2003).
- E. A. Davidson, M. B. David, J. N. Galloway, C. L. Goodale, R. Haeuber, J. A. Harrison, R. W. Howarth, D. B. Jaynes, R. R. Lowrance, N. B. Thomas, J. L. Peel, R. W. Pinder, E. Porter, C. S. Snyder, A. R. Townsend, M. H. Ward, Excess nitrogen in the US environment: Trends, risks, and solutions. *Issues Ecol.* **15**, 1–16 (2011).
- J. J. Yienger, H. Levy II, Empirical model of global soil-biogenic NO_x emissions. *J. Geophys. Res.* **100**, 11447–11464 (1995).
- E. A. Davidson, C. S. Potter, P. Schlesinger, S. A. Klooster, Model estimates of regional nitric oxide emissions from soils of the southeastern United States. *Ecol. Appl.* **8**, 748–759 (1998).
- L. Jaeglé, L. Steinberger, R. V. Martin, K. Chance, Global partitioning of NO_x sources using satellite observations: Relative roles of fossil fuel combustion, biomass burning and soil emissions. *Faraday Discuss.* **130**, 407–423 (2005).
- C. Wang, B. Z. Houlton, W. W. Dai, E. Bai, Growth in the global N₂ sink attributed to N fertilizer inputs over 1860 to 2000. *Sci. Total Environ.* **574**, 1044–1053 (2017).
- Y. Li, B. A. Schichtel, J. T. Walker, D. B. Schwede, X. Chen, C. M. B. Lehmann, M. A. Puchalski, D. A. Gay, J. L. Collett Jr., Increasing importance of deposition of reduced nitrogen in the United States. *Proc. Natl. Acad. Sci. U.S.A.* **113**, 5874–5879 (2016).
- Environmental Protection Agency, “Nitrogen Oxide Trends”; www.epa.gov/air-trends/nitrogen-dioxide-trends.
- T. P. Tomich, K. M. Scow, *The California Nitrogen Assessment: Challenges and Solutions for People, Agriculture, and the Environment* (University of California Press, 2016).
- A. R. Russell, L. C. Valin, E. J. Bucsela, M. O. Wenig, R. C. Cohen, Space-based constraints on spatial and temporal patterns of NO_x emissions in California, 2005–2008. *Environ. Sci. Technol.* **44**, 3608–3615 (2010).

12. R. C. Hudman, N. E. Moore, A. K. Mebust, R. V. Martin, A. R. Russell, L. C. Valin, R. C. Cohen, Steps towards a mechanistic model of global soil nitric oxide emissions: Implementation and space based-constraints. *Atmos. Chem. Phys.* **12**, 7779–7795 (2012).
13. P. Y. Oikawa, C. Ge, J. Wang, J. R. Eberwein, L. L. Liang, L. A. Allsman, D. A. Grantz, G. D. Jenerette, Unusually high soil nitrogen oxide emissions influence air quality in a high-temperature agricultural region. *Nat. Commun.* **6**, 8753 (2015).
14. P. A. Matson, M. Firestone, D. Herman, T. Billow, N. Kiang, T. Benning, J. Burns, "Agricultural systems in the San Joaquin Valley: Development of emissions estimates for nitrogen oxides" (Technical Report Contract No. 94-732, California Environmental Protection Agency, Air Resources Board, Technical Support Division, 1997).
15. M. Burger, W. R. Horwath, "Assessment of NO_x Emissions from Soil in California Cropping Systems" (Contract No. 09-329, 2013).
16. California Environmental Protection Agency - Air Resources Board, *The California Almanac of Emissions and Air Quality* (Sacramento, California, 2013); www.arb.ca.gov/aqd/almanac/almanac13/almanac13.htm.
17. E. Bai, B. Z. Houlton, Y. P. Wang, Isotopic identification of nitrogen hotspots across natural terrestrial ecosystems. *Biogeosciences* **9**, 3287–3304 (2012).
18. L. N. Ganzeveld, J. Lelieveld, F. J. Dentener, M. C. Krol, A. J. Bouwman, G.-J. Roelofs, Global soil-biogenic NO_x emissions and the role of canopy processes. *J. Geophys. Res. Atmos.* **107**, ACH 9-1–ACH 9-17 (2002).
19. D. Simpson, Biogenic VOC emissions in Europe: Modeling the implications for ozone control strategies, paper presented at the AWMA Conference, San Diego, CA, 8 to 14 November 1993.
20. M. K. Firestone, E. A. Davidson, Microbiological basis of NO and N₂O production and consumption in soil, in *Exchange of Trace Gases Between Terrestrial Ecosystems and the Atmosphere*, M. O. Andreae, David Steven Schimel, Eds. (Wiley, 1989), vol. 47, pp. 7–21.
21. I. C. Anderson, J. S. Levine, Simultaneous field measurements of biogenic emissions of nitric oxide and nitrous oxide. *J. Geophys. Res. Atmos.* **92**, 965–976 (1987).
22. E. J. Williams, G. L. Hutchinson, F. C. Fehsenfeld, NO_x and N₂O emissions from soil. *Global Biogeochem. Cycles* **6**, 351–388 (1992).
23. D. D. Parrish, E. J. Williams, D. W. Fahey, S. C. Liu, F. C. Fehsenfeld, Measurement of nitrogen oxide fluxes from soils: Intercomparison of enclosure and gradient measurement techniques. *J. Geophys. Res. Atmos.* **92**, 2165–2171 (1987).
24. E. J. Williams, D. D. Parrish, F. C. Fehsenfeld, Determination of nitrogen oxide emissions from soils: Results from a grassland site in Colorado, United States. *J. Geophys. Res. Atmos.* **92**, 2173–2179 (1987).
25. P. M. Homyak, J. C. Blankinship, K. Marchus, D. M. Lucero, J. O. Sickman, J. P. Schimel, Aridity and plant uptake interact to make dryland soils hotspots for nitric oxide (NO) emissions. *Proc. Natl. Acad. Sci. U.S.A.* **113**, E2608–E2616 (2016).
26. E. A. Davidson, W. Kingerlee, A global inventory of nitric oxide emissions from soils. *Nutr. Cycling Agroecosyst.* **48**, 37–50 (1997).
27. E. A. Davidson, Sources of nitric oxide and nitrous oxide following wetting of dry soil. *Soil Sci. Soc. Am. J.* **56**, 95–102 (1992).
28. M. E. Fenn, M. A. Poth, D. W. Johnson, Evidence for nitrogen saturation in the San Bernardino Mountains in southern California. *For. Ecol. Manage.* **82**, 211–230 (1996).
29. B. A. Hungate, C. P. Lund, H. L. Pearson, F. S. Chapin III, Elevated CO₂ and nutrient addition after soil N cycling and N trace gas fluxes with early season wet-up in a California annual grassland. *Biogeochemistry* **37**, 89–109 (1997).
30. I. C. Anderson, M. A. Poth, Semiannual losses of nitrogen as NO and N₂O from unburned and burned chaparral. *Global Biogeochem. Cycles* **3**, 121–135 (1989).
31. Environmental Protection Agency, "NAAQS Table"; www.epa.gov/criteria-air-pollutants/naaqs-table.
32. J. F. Trousdell, S. A. Conley, A. Post, I. C. Falooona, Observing entrainment mixing, photochemical ozone production, and regional methane emissions by aircraft using a simple mixed-layer framework. *Atmos. Chem. Phys.* **16**, 15433–15450 (2016).
33. California Environmental Protection Agency - Air Resources Board, "The California Emissions Projection Analysis Model", (Sacramento, California, 2013); www.arb.ca.gov/app/emsinv/fcemssumcat/fcemssumcat2016.php.
34. E. A. Davidson, M. Keller, H. E. Erickson, L. V. Verchot, E. Veldkamp, Testing a conceptual model of soil emissions of nitrous and nitric oxides: Using two functions based on soil nitrogen availability and soil water content, the hole-in-the-pipe model characterizes a large fraction of the observed variation of nitric oxide and nitrous oxide emissions from soils. *Bioscience* **50**, 667–680 (2000).
35. D. Tilman, J. Fargione, B. Wolff, C. D'Antonio, A. Dobson, R. Howarth, D. Schindler, W. H. Schlesinger, D. Simberloff, D. Swackhamer, Forecasting agriculturally driven global environmental change. *Science* **292**, 281–284 (2001).
36. R. Harrison, J. Webb, A review of the effect of N fertilizer type on gaseous emissions. *Adv. Agron.* **73**, 65–108 (2001).
37. P. A. Matson, R. Naylor, I. Ortiz-Monasterio, Integration of environmental, agronomic, and economic aspects of fertilizer management. *Science* **280**, 112–115 (1998).
38. K. L. McGeough, R. J. Laughlin, C. J. Watson, C. Müller, M. Ernfors, E. Cahalan, K. G. Richards, The effect of cattle slurry in combination with nitrate and the nitrification inhibitor dicyandiamide on in situ nitrous oxide and dinitrogen emissions. *Biogeosciences* **9**, 4909–4919 (2012).
39. K. A. Smith, D. R. Jackson, T. H. Misselbrook, B. F. Pain, R. A. Johnson, PA—Precision agriculture: Reduction of ammonia emission by slurry application techniques. *J. Agric. Eng. Res.* **77**, 277–287 (2000).
40. M. J. Helmers, J. L. Baker, Strategies for nitrate reduction: The Cedar River case study, paper presented at the Integrated Crop Management Conference, Iowa State University, Ames, Iowa, 1 to 2 December 2010.
41. H. J. Di, K. C. Cameron, R. R. Sherlock, Comparison of the effectiveness of a nitrification inhibitor, dicyandiamide, in reducing nitrous oxide emissions in four different soils under different climatic and management conditions. *Soil Use Manage.* **23**, 1–9 (2007).
42. M. A. Sutton, C. M. Howard, J. W. Erisman, G. Billen, A. Bleeker, P. Grennfelt, H. Van Grinsven, B. Grizzetti, *The European Nitrogen Assessment: Sources, Effects and Policy Perspectives* (Cambridge Univ. Press, 2011).
43. B. Z. Houlton, E. Boyer, A. Finzi, J. Galloway, A. Leach, D. Liptzin, J. Melillo, T. S. Rosenstock, D. Sobota, A. R. Townsend, Intentional versus unintentional nitrogen use in the United States: Trends, efficiency and implications. *Biogeochemistry* **114**, 11–23 (2013).
44. D. J. Sobota, J. E. Compton, M. L. McCrackin, S. Singh, Cost of reactive nitrogen release from human activities to the environment in the United States. *Environ. Res. Lett.* **10**, 025006 (2015).
45. B. Z. Houlton, E. Bai, Imprint of denitrifying bacteria on the global terrestrial biosphere. *Proc. Natl. Acad. Sci. U.S.A.* **106**, 21713–21716 (2009).
46. G. Van Drecht, A. F. Bouwman, J. M. Knoop, A. H. W. Beusen, C. R. Meinardi, Global modeling of the fate of nitrogen from point and nonpoint sources in soils, groundwater, and surface water. *Global Biogeochem. Cycles* **17**, 1115 (2003).
47. PRISM Climate Group, Oregon State University, <http://prism.oregonstate.edu>, created 4 February 2004.
48. G. Tonnesen, Z. Wang, M. Omary, C. J. Chien, "Assessment of Nitrogen Deposition: Modeling and Habitat Assessment," (CEC-500-2006-032, California Energy Commission, PIER Energy-Related Environmental Research, 2007).
49. G. R. Cass, S. Gharib, M. Peterson, J. W. Tilden, "The origin of ammonia emissions to the atmosphere in an urban area," (Open file report 82–6, Environmental Quality Laboratory, California, Institute of Technology, 1982).
50. D. H. Lenschow, P. B. Krummel, S. T. Siems, Measuring entrainment, divergence, and vorticity on the mesoscale from aircraft. *J. Atmos. Oceanic Tech.* **16**, 1384–1400 (1999).
51. S. R. Kawa, R. Pearson Jr., Ozone budgets from the dynamics and chemistry of marine stratocumulus experiment. *J. Geophys. Res.* **94**, 9809–9817 (1989).
52. A. Bandy, I. C. Falooona, B. W. Blomquist, B. J. Huebert, A. D. Clarke, S. G. Howell, R. L. Mauldin, C. A. Cantrell, J. G. Hudson, B. G. Heikes, J. T. Merrill, Y. Wang, D. W. O'Sullivan, W. Nadler, D. D. Davis, Pacific atmospheric sulfur experiment (PASE): Dynamics and chemistry of the south pacific tropical trade wind regime. *J. Atmos. Chem.* **68**, 5–25 (2011).
53. S. A. Conley, I. Falooona, G. H. Miller, D. H. Lenschow, B. Blomquist, A. Bandy, Closing the dimethyl sulfide budget in the tropical marine boundary layer during the pacific atmospheric sulfur experiment. *Atmos. Chem. Phys.* **9**, 8745–8756 (2009).
54. I. Falooona, S. A. Conley, B. Blomquist, A. D. Clarke, V. Kapustin, S. Howell, D. H. Lenschow, A. R. Bandy, Sulfur dioxide in the tropical marine boundary layer: Dry deposition and heterogeneous oxidation observed during the pacific atmospheric sulfur experiment. *J. Atmos. Chem.* **63**, 13–32 (2009).
55. J. B. Burkholder, *Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies. Evaluation No. 18, JPL Publication 15–10* (Jet Propulsion Laboratory, 2009); <http://jpldataeval.jpl.nasa.gov>.
56. W. H. Brune, B. C. Baier, J. Thomas, X. Ren, R. C. Cohen, S. E. Pusede, E. C. Browne, A. H. Goldstein, D. R. Gentner, F. N. Keutsch, J. A. Thornton, Ozone production chemistry in the presence of urban plumes. *Faraday Discuss.* **189**, 169–189 (2016).
57. T. Karl, P. K. Misztal, H. H. Jonsson, S. Shertz, A. H. Goldstein, A. B. Guenther, Airborne flux measurements of BVOCs above Californian oak forests: Experimental investigation of surface and entrainment fluxes, OH densities, and Damköhler numbers. *J. Atmos. Sci.* **70**, 3277–3287 (2013).
58. Soberanes Fires; http://cdfdata.fire.ca.gov/incidents/incidents_details_info?incident_id=1348.

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