

APPLIED ECOLOGY

Extrapolation of point measurements and fertilizer-only emission factors cannot capture statewide soil NO_x emissions

Maya Almaraz^{1*}†, Edith Bai^{2,3†}, Chao Wang², Justin Trousdell¹, Stephen Conley¹, Ian Faloona¹, Benjamin Z. Houlton^{1,4}

Maaz *et al.* argue that inconsistencies across scales of observation undermine our working hypothesis that soil NO_x emissions have been substantially overlooked in California; however, the core issues they raise are already discussed in our manuscript. We agree that point measurements cannot be reliably used to estimate statewide soil NO_x emissions—the principal motivation behind our new modeling/airplane approach. Maaz *et al.*'s presentation of fertilizer-based emission factors (a nonmechanistic scaling of point measures to regions based solely on estimated nitrogen fertilizer application rates) includes no data from California or other semiarid sites, and does not explicitly account for widely known controls of climate, soil, and moisture on soil NO_x fluxes. In contrast, our model includes all of these factors. Finally, the fertilizer sales data that Maaz *et al.* highlight are known to suffer from serious errors and do not offer a logically more robust pathway for spatial analysis of NO_x emissions from soil.

Our study was the first comprehensive, statewide, spatiotemporal analysis of soil NO_x emissions in California, which combined mass-balance modeling, flight data, and a comprehensive synthesis of point measurements going back several decades. Before our study, soil NO_x sources were either not considered or thought to be quantitatively unimportant in California's NO_x budget. However, this perception was based on scant information and a small set of chamber measurements. Using our model and flight data, we identified substantial spatial patterns in soil NO_x sources and found that fertilized cropland soils accounted for 20 to 32% of statewide NO_x emissions. We performed a robust sensitivity analysis of our model, which showed that climate (which varied over time in our model) was the most important control over variation in NO_x fluxes, followed by soil texture. The airplane flight data and NO_x inversion analysis pointed to a soil NO_x source that was quantitatively consistent with our model predictions. We already discussed the strengths and weaknesses of each approach, inclusive of our synthesis of point measures based on soil chambers, in our manuscript and subsequent eLetter (<http://advances.sciencemag.org/content/4/1/eaao3477/tab-e-letters>).

Maaz *et al.* contend that discrepancies between local chamber measurements and our results undermine our study's working hypothesis; however, the authors do not provide evidence that disproves our results. If anything, Maaz *et al.*'s reliance on chamber-based information and extrapolation of fertilizer-based NO_x emission factors is justifiably inadequate for examining spatiotemporal patterns of soil NO_x emissions across natural and managed environments. Furthermore, Maaz *et al.*'s meta-analysis of fertilizer-based NO_x emission factors includes no data from California or other semiarid sites.

¹Department of Land, Air, and Water Resources, University of California–Davis, Davis, CA 95616, USA. ²Key Laboratory of Forest and Management, Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, China. ³School of Geographical Sciences, Northeast Normal University, Changchun 130024, China. ⁴John Muir Institute of the Environment, University of California–Davis, Davis, CA 95616, USA.

*Corresponding author. Email: mayaalmaraz@gmail.com

†These authors contributed equally to this work.

Copyright © 2018
The Authors, some
rights reserved;
exclusive licensee
American Association
for the Advancement
of Science. No claim to
original U.S. Government
Works. Distributed
under a Creative
Commons Attribution
NonCommercial
License 4.0 (CC BY-NC).

Maaz *et al.* argue that point measurements are inadequate for scaling-up statewide NO_x emissions, a notion with which we are in agreement. This weakness is principal to our motivation to move beyond bulk emission factors, which are based on relationships between point measurements and fertilizer N input rates. The most robust use of point measurements, we contend, is in mechanistic understanding of soil NO_x production rates—systematically manipulating controls at local scales to build new concepts and algorithms. In addition, our model does just that, allowing for known controls such as soil texture, climate, carbon, and nitrogen input rates to affect spatial and temporal patterns of soil NO_x emissions. This does not mean that our results are free from uncertainty; as with any model, there are important uncertainties to consider, which we highlighted in the sensitivity analysis and range of results reported. Nevertheless, our model is a significant advance beyond the bulk emission factors proposed by Maaz *et al.*, which do not include controls on soil NO_x emissions and rely on scaling point measurements to regional scales.

Further, as Maaz *et al.* indicate, we performed a comprehensive synthesis of point measurements over several decades and noted cases of agreement and disagreement with the model (table 1 in the original manuscript). Given the unaccounted-for errors in scaling point measurements, lack of mechanisms and mass-balance constraints, and wholly inadequate spatial and temporal coverage of existing measurements, we performed this analysis for reference but did not use it to quantify NO_x emissions (where we relied on the model and airplane data).

Quantitatively, the significant advance in our study is the combined use of spatiotemporal modeling and airplane measurements, the latter of which takes into account a similar footprint to that of the modeled estimates. The scales are aligned in these approaches. We find extremely strong correspondence between the model and flight data. More work using this approach will be essential to further understand the spatial and temporal patterns of soil NO_x emissions and for separating out other sources, including fossil fuel combustion and seasonal fire emissions.

As Maaz *et al.* noted, we reported mean emissions of 19.8 kg N ha⁻¹ year⁻¹; however, this value does not take into account canopy

uptake (discussed in the manuscript), which would reduce the value to 9.9 kg N ha⁻¹ year⁻¹, generating a net mean emission factor of 7.5%. The highly skewed nature of NO_x emissions generated by our model (depicted in Fig. 1) demonstrates why the median may be a more statistically appropriate value for describing these data. Median values were between ~6 and 12 kg N ha⁻¹ year⁻¹ (with and without canopy uptake, respectively), generating emission factors of 4.6 to 9.1%. Irrigation, fixation, and N deposition can be important inputs to agricultural systems (Table 1). Considering a complete mass balance that parses NO_x emissions versus all N inputs, the fractional contribution of soil NO_x emissions decreases even further (3.2% on the low end and 10.5% on the high end).

Most critically, the two meta-analyses referred to by Maaz *et al.* do not have a single data point collected from California, or from arid or semiarid ecosystems (1, 2), which encompass much of California's agriculture. Isotopic evidence and models point to the highest relative gaseous losses of N from semiarid/drier environments, with NO_x being especially important (3–6). Data that we compiled in California reveals higher emission factors than the global mean cited by Maaz *et al.*, with Burger and Horwath (7) averaging an emission factor of 1.2% in the Sacramento region (consistent with lower NO_x that we simulate

for this region) and Matson *et al.* (8) averaging an emission factor of 3.4% in the Central Valley. Further, in the most recent experimental study in California's Imperial Valley, where our model points to the highest emissions, Oikawa *et al.* (9) present an integrated emission factor of 1.8 to 6.6% (~11%, if averaged across both small and large field measurements). These findings are consistent with several lines of evidence for higher NO_x in this region generated by our model estimates, satellite data, and point measurements (9, 10). Together, these data suggest a gradient whereby emission factors increase in the hottest and driest areas of California. Beyond California, Barton *et al.* (11) derived an N₂O emission factor in arid agricultural soils of Australia that was 60 times lower than the Intergovernmental Panel on Climate Change default factor. The reason is consistent with our model; NO_x production is favored above that of N₂O in dry arid climates, so there is a mechanistic reason to expect that emission factors may differ in these ecosystems [see (5) for the compilation of NO_x/N₂O data versus WFPS (water-filled pore space)].

Maaz *et al.* argue that the fertilizer data we used did not match fertilizer sales data; however, this phenomenon has already been documented elsewhere, and application of these data would likely increase, not decrease, our model-based estimates. For example, Rosenstock *et al.* (12) show that, while fertilizer sales data disagree with those of fertilizer use, recommended guidelines agree much better with use data. A comparison of the fertilizer data we used agrees well with recommendations by the California Department of Food and Agriculture (Fig. 2). Furthermore, Rosenstock *et al.* (12) estimate that average N fertilizer inputs across crops in 2005 were 144 kg N ha⁻¹ year⁻¹, similar to our estimates of 131.8 kg N ha⁻¹ year⁻¹. In addition, our mass balance nitrogen use efficiency estimates were also consistent with or higher (likely because we are missing N from manure and multiple rotations) than the mean for the entire United States (13).

In addition, our model does not take into account changes in fertilizer use over time (we used an amalgamation of fertilizer data from 1964 to 2006); however, we hypothesize that observed increases in cropland and population size will covary with increases in fertilizer, resulting in increased NO_x emissions since the report of Matson *et al.* (8). We did not consider multiple crop rotations either, which are not

Table 1. Nitrogen budget in cropland area for soil model from Almaraz *et al.* (15) (average mass balance data are preliminary estimates in preparation).

Flux	Mean (kg N ha ⁻¹ year ⁻¹)
Deposition	8.64
Irrigation	6.73
Fixation	41.8
Fertilizer	131.8
Harvest	100.4
Ammonia	5.39
Leaching	36.8
Denitrification	36.2

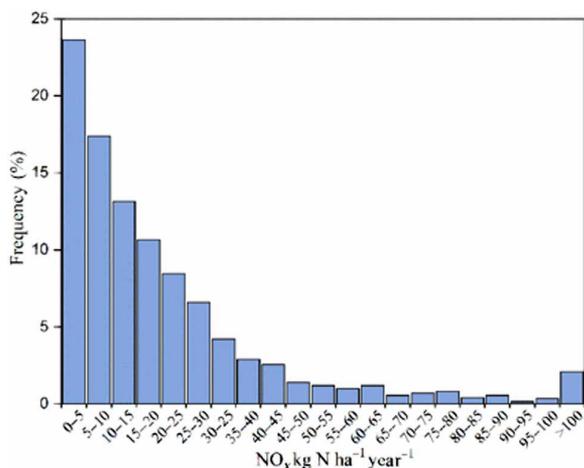


Fig. 1. Frequency distribution of modeled NO_x emissions (kg of N ha⁻¹ year⁻¹) in each grid cell (4000 m × 4000 m) in croplands of California.

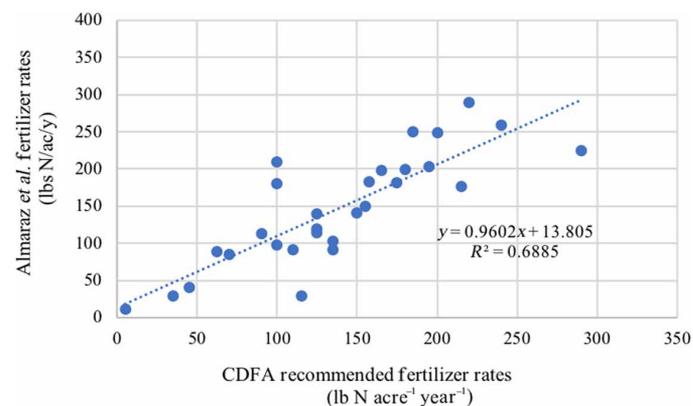


Fig. 2. Recommended nitrogen fertilizer inputs by the California Department of Food and Agriculture's Fertilizer Research and Education Program compared to nitrogen fertilizer inputs used in Almaraz *et al.*, 2018. CDFFA, California Department of Food and Agriculture.

uncommon in California, and which are likely to require higher fertilizer applications than the ones we used in the model, nor did we consider manure, which may account for as much as 35% of fertilizer inputs in California (14).

Finally, our preliminary analysis of the mass balance of N using our model is consistent with other studies, implying that ~50% of the N enters the crop and the remainder is lost to the atmosphere and hydrosphere (Table 1). Recognizing that we did not consider N inputs via manure and multiple-fertilizer additions, there is reason to suspect that we may be underestimating total emissions from California agriculture. Alternatively, newer practices that use micro-fertigation and other techniques that improve nitrogen use efficiency could have the opposite effect—demonstrating an area where further research is needed, with new approaches such as satellite, airplane data, and improved modeling coupled with strategic manipulation of variables, such that we might be able to move beyond extrapolations of point measurements and nonmechanistic application of emission factors.

REFERENCES AND NOTES

- A. F. Bouwman, L. J. M. Boumans, N. H. Batjes, Satellite measurements of daily variations in soil NO_x emissions. *Geophys. Res. Lett.* **32**, 28-1–28-9 (2002).
- S. Liu, F. Lin, S. Wu, C. Ji, Y. Sun, Y. Jin, S. Li, Z. Li, J. Zou, Modeling global annual N₂O and NO emissions from fertilized fields. *Global Biogeochem. Cycles* **16**, 2520–2532 (2017).
- R. Amundson, A. T. Austin, E. A. G. Schuur, K. Yoo, V. Matzek, C. Kendall, A. Uebesax, D. Brenner, W. T. Baisden, Global patterns of the isotopic composition of soil and plant nitrogen. *Global Biogeochem. Cycles* **17**, 31 (2003).
- B. Z. Houlton, D. M. Sigman, L. O. Hedin, Isotopic evidence for large gaseous nitrogen losses from tropical rainforests. *Proc. Natl. Acad. Sci. U.S.A.* **103**, 8745–8750 (2006).
- E. Bai, B. Z. Houlton, Y. P. Wang, Isotopic identification of nitrogen hotspots across natural terrestrial ecosystems. *Biogeosciences* **9**, 3287–3304 (2012).
- F. M. Soper, T. W. Boutton, P. M. Groffman, J. P. Sparks, Nitrogen trace gas fluxes from a semiarid subtropical savanna under woody legume encroachment. *Global Biogeochem. Cycles* **30**, 614–628 (2016).
- M. Burger, W. R. Horwath, *Assessment of NO_x Emissions from Soil in California Cropping Systems* (University of California, Davis, 2013).
- 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* (California Environmental Protection Agency, Air Resources Board, Technical Support Division, 1997).
- 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).
- G. C. M. Vinken, K. F. Boersma, J. D. Maasakkers, M. Adon, R. V. Martin, Worldwide biogenic soil NO_x emissions inferred from OMI NO₂ observations. *Atmos. Chem. Phys.* **14**, 10363–10381 (2014).
- L. Barton, R. Kiese, D. Gatter, K. Butterbach-Bahl, R. Buck, C. Hinz, D. V. Murphy, Nitrous oxide emissions from a cropped soil in a semi-arid climate. *Global Change Biol.* **14**, 177–192 (2008).
- T. Rosenstock, D. Liptzin, J. Six, T. Tomich, Nitrogen fertilizer use in California: Assessing the data, trends and a way forward. *Calif. Agric.* **67**, 68–79 (2013).
- 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).
- T. P. Tomich, S. B. Brodt, R. A. Dahlgren, K. M. Scow, Eds., *The California Nitrogen Assessment: Challenges and Solutions for People, Agriculture, and the Environment* (University of California Press, 2016).
- M. Almaraz, E. Bai, C. Wang, J. Trousdell, S. Conley, I. Faloona, B. Z. Houlton, Agriculture is a major source of NO_x pollution in California. *Sci. Adv.* **4**, eaau3477 (2018).

Acknowledgments: We thank T. O'Green and D. Liptzin for their assistance with data acquisition and S. Chen for sharing her Weather Research and Forecasting modeling runs.

Funding: This work was supported by the National Science Foundation Postdoctoral Research Fellowship in Biology (1611895), the Major State Basic Research Development Program of China (2014CB954400), a National Science Foundation Career Grant (1411368), and the Dave and Lucile Packard Foundation. I.F. was supported in part by the California Agricultural Experiment Station, Hatch project CA-D-LAW-2229-H. The airborne NO_x measurements were supported by a grant sponsored by the U.S. Environmental Protection Agency through the Bay Area Air Quality Management District (grant no. 2016-129) for the California Air Resource Board's CABOTS (California Baseline Ozone Transport Study) project.

Author contributions: M.A., E.B., and B.Z.H. conceived the research and designed the study. M.A. collected literature data on NO_x observations recorded in California. E.B. and B.Z.H. developed the model. E.B. and C.W. generated model estimates of soil NO_x emissions. I.F., J.T., and S.C. performed airborne measurements of NO_x and generated estimates of soil NO_x emissions for the Central Valley in California. M.A. led manuscript preparation with input from all coauthors. **Competing interests:** The authors declare that they have no competing interests. **Data and materials availability:** All data needed to evaluate the conclusions in the paper are present in the paper. Additional data related to this paper may be requested from the corresponding author.

Submitted 18 July 2018

Accepted 31 July 2018

Published 12 September 2018

10.1126/sciadv.aau7373

Citation: M. Almaraz, E. Bai, C. Wang, J. Trousdell, S. Conley, I. Faloona, B. Z. Houlton, Extrapolation of point measurements and fertilizer-only emission factors cannot capture statewide soil NO_x emissions. *Sci. Adv.* **4**, eaau7373 (2018).

Extrapolation of point measurements and fertilizer-only emission factors cannot capture statewide soil NO_x emissions

Maya Almaraz, Edith Bai, Chao Wang, Justin Trousdell, Stephen Conley, Ian Faloona and Benjamin Z. Houlton

Sci Adv 4 (9), eaau7373.
DOI: 10.1126/sciadv.aau7373

ARTICLE TOOLS <http://advances.sciencemag.org/content/4/9/eaau7373>

REFERENCES This article cites 12 articles, 2 of which you can access for free
<http://advances.sciencemag.org/content/4/9/eaau7373#BIBL>

PERMISSIONS <http://www.sciencemag.org/help/reprints-and-permissions>

Use of this article is subject to the [Terms of Service](#)

Science Advances (ISSN 2375-2548) is published by the American Association for the Advancement of Science, 1200 New York Avenue NW, Washington, DC 20005. The title *Science Advances* is a registered trademark of AAAS.

Copyright © 2018 The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. No claim to original U.S. Government Works. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC).