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

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Maaz et al. argue that inconsistencies across scales of observation undermine our working hypothesis that soil NOx 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 NOx 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 NOx 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 NOx emissions from soil.

Our study was the first comprehensive, statewide, spatiotemporal analysis of soil NOx 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 NOx sources were either not considered or thought to be quantitatively unimportant in California’s NOx 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 NOx sources and found that fertilized cropland soils accounted for 20 to 32% of statewide NOx 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 NOx fluxes, followed by soil texture. The airplane flight data and NOx inversion analysis pointed to a soil NOx 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 e-Letter (http://advances.sciencemag.org/content/4/1/eaao3477/1).

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 NOx emission factors is justifiably inadequate for examining spatiotemporal patterns of soil NOx emissions across natural and managed environments. Furthermore, Maaz et al.’s meta-analysis of fertilizer-based NOx emission factors includes no data from California or other semiarid sites.

Maaz et al. argue that point measurements are inadequate for scaling-up statewide NOx 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 NOx 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 NOx 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 NOx 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 NOx 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 NOx 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 NO₃ 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 budget to agricultural systems (Table 1), fixation, and N deposition can be important inputs to agricultural systems (Table 1). Considering a complete mass budget to agricultural systems (Table 1). Considering a complete mass balance that parses NO₃ emissions versus all N inputs, the fractional contribution of soil NO₃ 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 semi-arid ecosystems (1, 2), which encompass much of California’s agriculture. Isotopic evidence and models point to the highest relative gaseous losses of N from semi-arid/drier environments, with NO₃ 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 NO₃ 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 NO₃ 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; NO₃ 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 NO₃/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 NO₃ emissions since the report of Matson et al. (8). We did not consider multiple crop rotations either, which are not

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**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                |

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**Fig. 1. Frequency distribution of modeled NO₃ emissions (kg of N ha⁻¹ year⁻¹) in each grid cell (4000 m x 4000 m) in croplands of California.**

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**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. CDFA, 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-fertilization 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.

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Author contributions: M.A. collected literature data on NOx emissions inferred from OMI NO2 observations recorded in California. E.B. and B.Z.H. developed the model. E.B. and C.W. generated model estimates of soil NOx emissions. I.F., J.T., and S.C. performed airborne measurements of NOx and generated estimates of soil NOx 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.