Global metaanalysis of the nonlinear response of soil nitrous oxide (N_2O) emissions to fertilizer nitrogen

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Nitrous oxide (N_2O) is a potent greenhouse gas (GHG) that also depletes stratospheric ozone. Nitrogen (N) fertilizer rate is the best single predictor of N_2O emissions from agricultural soils, which are responsible for ~50% of the total global anthropogenic flux, but it is a relatively imprecise estimator. Accumulating evidence suggests that the emission response to increasing N input is exponential rather than linear, as assumed by Intergovernmental Panel on Climate Change methodologies. We performed a metaanalysis to test the generalizability of this pattern. From 78 published studies (233 site-years) with at least three N-input levels, we calculated N_2O emission factors (EFs) for each nonzero input level as a percentage of N input converted to N_2O emissions. We found that the N_2O response to N inputs grew significantly faster than linear for synthetic fertilizers and for most crop types. N-fixing crops had a higher rate of change in EF (ΔEF) than others. A higher ΔEF was also evident in soils with carbon >1.5% and soils with pH <7, and where fertilizer was applied only once annually. Our results suggest a general trend of exponentially increasing N_2O emissions as N inputs increase to exceed crop needs. Use of this knowledge in GHG inventories should improve assessments of fertilizer-derived N_2O emissions, help address disparities in the global N_2O budget, and refine the accuracy of N_2O mitigation protocols. In low-input systems typical of sub-Saharan Africa, for example, modest N additions will have little impact on estimated N_2O emissions, whereas equivalent additions (or reductions) in excessively fertilized systems will have a disproportionately major impact.

fertilizer response | greenhouse gas emissions | agriculture | bioenergy | greenhouse gas mitigation

Nitrous oxide (N_2O) is a major greenhouse gas (GHG) with a global warming potential ~300-fold that of CO_2 over a 100-y time period (1). Additionally, N_2O is the largest stratospheric ozone-depleting substance and is projected to remain so for the remainder of this century (2). N_2O emissions from agricultural soils, produced predominantly by the microbial processes of nitrification (oxidation of ammonium to nitrate) and denitrification (reduction of nitrate via N_2O to N_2) (3), constitute ~50% of global anthropogenic N_2O emissions (1), primarily as a result of the addition of synthetic nitrogen (N) fertilizers and animal manure to soil (4). The total input of N to soil, and its subsequent availability, is a robust predictor of N_2O fluxes and has been used to construct most national GHG inventories using an N_2O emission factor (EF) approach (5).

The N_2O EF is the percentage of fertilizer N applied that is transformed into fertilizer-induced emissions, which is calculated for Intergovernmental Panel on Climate Change (IPCC) GHG inventories as the difference in emission between fertilized and unfertilized soil under otherwise identical conditions. Global EFs for fertilizer-induced direct N_2O emissions have been determined by Eichner (6), Bouwman (7, 8), Mosier et al. (9), Bouwman et al. (4, 10), and Stehfest and Bouwman (11). The current global mean value, derived from over 1,000 field measurements of N_2O emissions, is ~0.9% (10, 11). This value for fertilizer-induced emissions is an approximate average of emissions induced by synthetic fertilizer (1.0%) and animal manure (0.8%), and it has been rounded by the IPCC (5) to 1% due to uncertainties and the inclusion of other N inputs, such as crop residues (12) and soil organic matter mineralization (1). In short, for every 100 kg of N input, 1.0 kg of N in the form of N_2O is estimated to be emitted directly from soil.

A 1% EF assumes a linear relationship between N input and N_2O emissions that is indifferent to biological thresholds that might occur, for example, when the availability of soil inorganic N exceeds crop N demands. Because the vast majority of studies on N_2O emissions from crops have examined a single fertilizer input (many without a zero N control), there is no power in these studies for detecting such thresholds. However, results from a growing number of field experiments with multiple N fertilizer rates indicate that emissions of N_2O respond in an exponentially increasing manner to increasing N inputs across a range of fertilizer formulations, climates, and soil types (e.g., refs. 13–16), suggesting that EFs are not constant but increase monotonically with N additions.

Incorporating this knowledge into large-scale N_2O models could help to close the gap between bottom-up and top-down estimates of fertilizer N_2O contributions to regional and global fluxes (17, 18). Bottom-up estimates rely on the extrapolation of flux chamber measurements in individual ecosystems to larger regions, including the globe. Grace et al. (19), for example, used a nonlinear N_2O emission function to model total direct N_2O emissions from the US north central region between 1964 and 2005. Their estimate was equivalent to an EF of 1.75% over this period, which is substantially higher than the global default IPCC value of 1%. More recently, Griffis et al. (20) used tall tower eddy covariance measurements to estimate an overall US north central region EF of 1.8% for contemporary fluxes.

Top-down estimates are based on changes in atmospheric N_2O concentrations over time that are assigned to changes in human activities known to affect N_2O fluxes. Global top-down estimates of N_2O from anthropogenic sources of reactive N, including

Significance

We clarify the response of the greenhouse gas nitrous oxide (N_2O) to nitrogen (N) fertilizer additions, a topic of considerable debate. Previous analyses have used single N-rate experiments to define a linear response to N additions across climate, management, and soil conditions globally. Here, we provide a first quantitative comparison of N_2O emissions for all available studies that have used multiple N rates. Results show that a nonlinear emission factor better represents global emission patterns with lower uncertainty, offering more power for balancing the global N_2O budget and for designing effective mitigation strategies.

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animal manure (21), yield an overall EF of 4 ± 1% (17, 18). Although bottom-up models are in broad agreement (22), there are large uncertainties and the agreement breaks down at regional and subregional scales (23). The use of EFs that vary with N input may help to reconcile this difference and guide policies that are urgently needed to curb the projected 20% increase in agricultural N_2O emissions expected by 2030 (23).

Nonlinear EFs also hold implications for estimated N_2O fluxes from low-input cropping systems typical of those in sub-Saharan Africa. If N_2O emissions are not much affected by fertilizer N added to meet crop needs precisely, then modest fertilizer additions will have little impact on estimated N_2O emissions. Impacts will be far larger, on the other hand, where N is added at rates that exceed crop N needs.

Response curves for N_2O flux as a function of N input have recently become more common. McSwiney and Robertson (13), for example, reported an exponentially increasing N_2O response to N fertilizer along a nine-point fertilizer N gradient for nonirrigated corn in Michigan. In their study, N_2O fluxes following fertilization more than doubled (20 vs. >50 g of N_2O-N $ha^{-1} \cdot d^{-1}$) at N inputs greater than 100 $kg \cdot ha^{-1}$, the level at which yield was maximized. Hoben et al. (15) documented a similar response for five on-farm sites in Michigan under corn-soybean rotations with six fertilizer N inputs (0–225 $kg \cdot ha^{-1}$). Others (14, 16), but not all (24), have since found similar patterns for multiple N-input levels. Kim et al. (25) documented 18 published instances with nonlinear responses to four or more levels.

Here, we test the generality of these findings globally. Although there are very few N_2O response studies with a sufficient number of N-input levels to characterize a nonlinear response with precision, we located over 200 studies with two or more N inputs in addition to a zero N control, which allows the determination of two or more EFs for the same site-year. We then evaluated the presence and direction of a slope, and calculated ΔEF as the percent change in EF per unit of additional N input (measured in kilograms per hectare). Here, we report the results of a metaanalysis of this global dataset and investigate the potential interaction of ΔEF with other factors, such as crop type, fertilizer type, and available environmental factors. We also test for possible biases in sampling factors, including the duration and number of measurements, flux chamber area, number of samples per flux measurement, and numbers of replicates. We then compare results with published EF determinations, including those used as a basis for current IPCC tier 1 methodologies (4, 10) and carbon credit markets (26, 27).

Results

We identified (Tables S1 and S2 and Dataset S1) 78 papers, covering 84 locations (Fig. 1) and 233 site-years, that satisfied our selection criteria of in situ flux measurements from sites fertilized at three or more N input levels, including a zero N control. A Kolmogorov–Smirnov test confirmed that ΔEFs are not normally distributed ($P < 0.0001$; Fig. S1). In 156 cases (67%), ΔEFs are positive; in the remainder, they are zero or negative. A resampling procedure on all ΔEFs showed that the mean (0.0027) and median (0.0005) ΔEFs are positive, with 95% confidence intervals (CIs) of 0.0011–0.0044 and 0.0003–0.0009, respectively. Removing four outlier site-years from the dataset (two positive and two negative values) slightly decreased the mean ΔEF (to 0.0024), decreased the SE substantially (37%), but did not affect the median ΔEF or its SE (Fig. 2*A* and Table S3).

N-fixing crops, upland grain crops, rice, and perennial grass/forage crops all had positive ΔEFs ($P < 0.01$; Fig. 2*A* and Table S3). N-fixing crops (including those in rotation with other crops) had the highest mean ΔEF (0.018), followed by perennial grass/forage crops (0.0033), upland grain crops (0.0017), and rice (0.001). The ΔEF for bare soil was 0.031 based on a single study (one site-year). The only significant difference among crop types was N-fixing crops vs. (*i*) non–N-fixing crops ($P = 0.001$), (*ii*) upland grain crops ($P = 0.001$), (*iii*) rice ($P = 0.0006$), and (*iv*) perennial grass/forage crops ($P = 0.004$) (Table S4). All of these tests remained significant after a Benjamini and Hochberg (BH) adjustment (28) for the total number of tests.

Fig. 1. Location of study sites included in the metaanalysis ($n = 84$ locations).

Synthetic fertilizers ($n = 188$, including organic formulations) dominated other available fertilizer types (manure, $n = 16$; mixture of synthetic and manure, $n = 10$), with a mean ΔEF (0.0027; Fig. 2*B* and Table S3) similar to the mean ΔEF for all site-years. Among synthetic fertilizers, ammonium nitrate (AN) and urea had positive mean ΔEFs ($P < 0.002$), whereas calcium ammonium nitrate (CAN), controlled-release urea (CRU), urea ammonium nitrate (UAN), manure, and mixed fertilizer (Mixed) had ΔEFs not different from zero. A difference (*t* test) among synthetic fertilizers (Table S5) showed that mean ΔEFs for AN were higher ($P < 0.01$) than mean ΔEFs for CAN, UAN, and CRU; the ΔEF for urea was higher ($P = 0.0034$) than for CRU. BH adjustment leaves all differences significant at the $P < 0.05$ level.

Among available environmental and fertilizer management factors, ΔEFs were positive and somewhat higher where soil organic carbon (SOC) contents were >1.5% (to 6.7% with one exception at 35%), where soil pH was ≤7, and where fertilizer was applied only once per year rather than split-applied in two or more applications (Fig. 2*C* and Tables S3 and S6).

The average EF for site-year was positively correlated with ΔEF (adjusted $r^2 = 0.22$; Fig. S2), with a slope of 0.0024 (±0.0003 SE). Site-years with a lowest nonzero N input of <100 $kg \cdot ha^{-1}$ had a mean ΔEF (0.0034) larger ($P = 0.007$; Fig. 2*C*) than the mean ΔEF for the site-years with a lowest nonzero N input of >100 $kg \cdot ha^{-1}$ (0.0009). Both groups have mean ΔEFs larger than zero ($P = 5 \times 10^{-5}$ and $P = 0.01$, respectively).

Among sampling-related factors, the number of measurements, duration of the experiment, number of replicates, and number of samples per flux measurement did not affect the mean ΔEF at the 95% confidence level (Fig. S3 and Table S7). Chamber area was the exception, with large chambers (>0.2 m^2, equivalent to 45 × 45-cm square) corresponding to lower mean ΔEF ($P < 0.0003$) compared with smaller chambers (<0.2 m^2). Sites with three or more nonzero N input rates showed no significant relationship between ΔEF and adjusted r^2 of the quadratic function fit (Fig. S4).

The largest experimental factor associations in contingency tables (Table S8) were between mean annual temperature and SOC (ϕ = −0.59), between mean annual temperature and soil pH (ϕ = 0.44), and between SOC and soil pH (ϕ = −0.36). The sampling factors (Table S9) had strongest associations between chamber area and number of replicates (ϕ = −0.55) and between number of measurements and duration of the experiment (ϕ = 0.44).

Discussion

Our results show that N_2O emissions tend to grow in response to N fertilizer additions at a rate significantly greater than linear; that is, we found a positive mean ΔEF for all site-years as well as for the majority of groupings by crop; type of N fertilizer applied; and other environmental, management, and sampling factors (Fig. 2). This

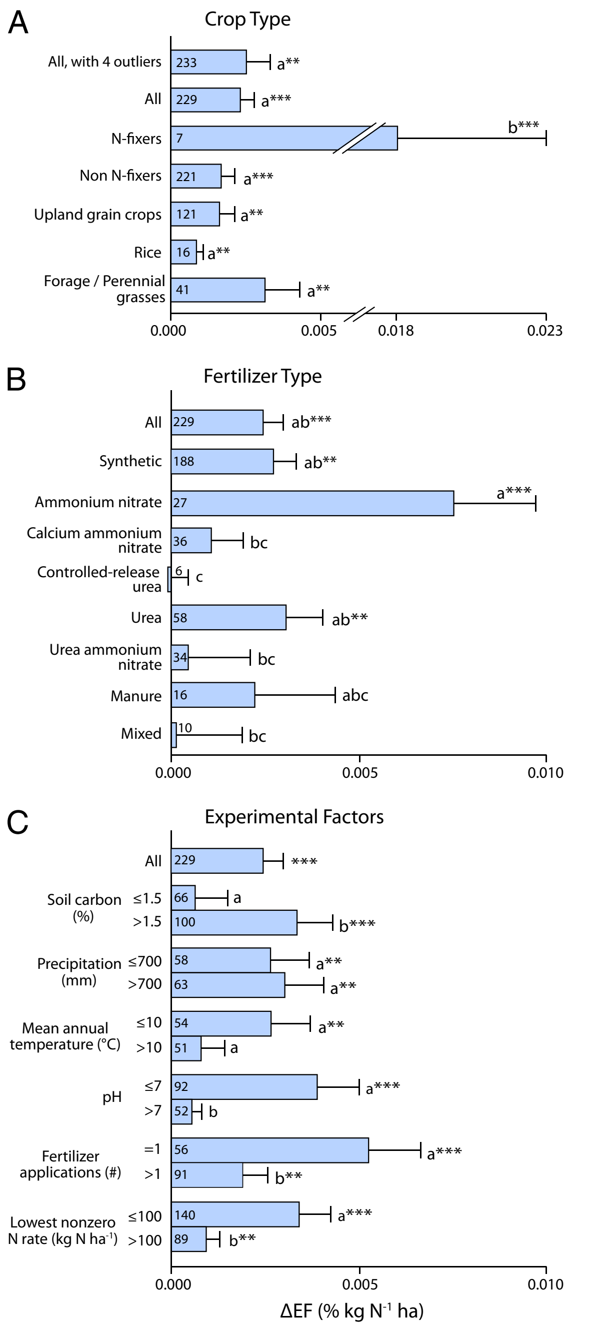

Fig. 2. ΔEF by crop type (*A*), fertilizer type (*B*), and other experimental factors (*C*). Data are presented as mean ± SEM, with *n* noted at the base of each bar. Asterisks indicate significant differences from zero (****P* < 0.001; ***P* < 0.01). For crop (*A*) and fertilizer (*B*) types, different letters indicate significant differences between mean ΔEFs for groups of site-years within each category; for experimental factors (*C*), different letters indicate significant pairwise differences between factors. Note the *x*-axis scale break in *A*.

main result is in agreement with results from most studies with five or more N-input levels (13, 15, 25) and suggests that the current global N_2O EF of 1% (5) is too conservative for high N-input rates.

Only N-fixing crops had a ΔEF larger than the other crop groups (upland grains, rice, and perennial grasses; Fig. 2*A*), which is likely a result of the low N fertilizer needs of N fixers. That a single bare soil site had an even higher ΔEF (0.031; Table S3) further supports the interpretation that N_2O emissions are accelerated in soils fertilized in excess of crop requirements. In contrast, ΔEF was significantly lower for CRU than for other synthetic fertilizers and also lower (but not significantly) for split fertilizer applications vs. single applications (Table S3). A lower ΔEF means that N_2O emissions are decelerated, which is consistent with the slower N delivery rate of CRU and multiple fertilizer applications. Collectively, these findings support the hypothesis that plant-heterotroph competition exerts control on the rate of N_2O emission, which is consistent with the N surplus approach of van Groenigen et al. (29). Site-years with a pH below 7 had both higher mean EF and mean ΔEF; given the positive correlation between ΔEF and mean EF (Fig. S2), this finding is consistent with higher N_2O emissions from lower pH soils.

Chamber size was the only sampling factor that showed significant differences in ΔEF: Chambers larger than 0.2 m^2 (~45 × 45 cm on a side if square) had somewhat lower ΔEFs than smaller chambers. Contingency tables did not reveal strong associations between experimental and sampling factors (Tables S8 and S9), which means that different experimental or sampling factors are independent. However, one source of potential bias is that site-years with a lowest nonzero N input <100 $kg \cdot ha^{-1}$ are associated with higher ΔEFs compared with site-years with a lowest N input >100 $kg \cdot ha^{-1}$ (Fig. 2*C*). This result is likely because for many of these experiments, the lowest nonzero N input surpasses the crop N saturation point, obscuring what might otherwise be a more positive ΔEF. Another potential source of bias is the small number of studies with multiple N rates (Table S3), which probably explains our inability to detect the difference in ΔEFs with an increasing number of N levels (Fig. S3). The quality of data did not decline with increasing ΔEF (Fig. S4).

The significant presence of negative ΔEFs (i.e., a slower than linear emission growth rate with N input; Fig. S1) does not have a satisfactory theoretical explanation. Such a response seems to imply that at higher N inputs, plants use N more efficiently, which has never been observed. Another explanation is that on a molar basis, microbes produce more N_2 relative to N_2O at higher levels of N input, but this conflicts with our understanding of the microbiological basis for N_2O production (30). The remaining explanation is that negative ΔEFs arise from high spatial and temporal variability in N_2O emissions. Were we to exclude site-years with negative ΔEFs from the metaanalysis, the emission response to N input would become even more nonlinear.

Our findings agree in general with most prior work. Bouwman et al. (10) assumed an exponential relationship between N_2O emissions and N input in their model, but the majority of their site-years had a single N input and only a few had a zero N control. Our analysis explicitly tests the changes in EF for each experiment with multiple N input levels, arriving at the same general conclusion of a faster than linear N_2O emission increase but with a quantitative and higher confidence outcome.

Our ΔEF model, when excluding N fixers and the site with bare soil, has a much narrower CI compared with IPCC tier 1 methodology (Fig. 3). Philibert et al. (30) show an improved CI for the range of nonlinear and linear models. When not accounting for parameter uncertainty, the lower boundary of Philibert et al. (31) coincides with ours, whereas the upper boundary is more conservative than ours for N-input levels >150 $kg \cdot ha^{-1}$. Parameter uncertainty widens the CI in the work by Philibert et al. (31) and brings our estimate entirely within the boundary for N inputs up to 250 $kg \cdot ha^{-1}$.

Kim et al. (25) did not estimate the degree of EF nonlinearity in their dataset but provided a robust qualitative assessment of EF behavior that showed 6 linear, 18 exponential, and 2 hyperbolic responses out of 26 total studies. Using the same technique on the subset of our site-years with more than three nonzero N inputs yields 30 linear, 55 exponential, and 11 hyperbolic EF responses, which is in good agreement.

Hoben et al. (15) provided a strong case for a faster than linear N_2O emission increase for US midwestern maize crops with a model based on log-transformed values to make emission estimates more conservative. This model forms the basis for

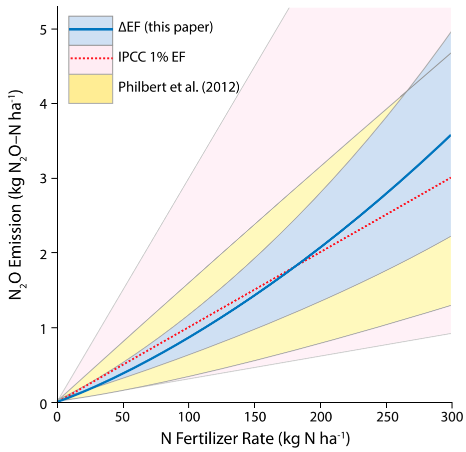

Fig. 3. Comparison of the uncertainties associated with IPCC tier 1 (1%), a range of six models from Philibert et al. (31), and the mean ΔEF model for all site-years from this metaanalysis (excluding N-fixing crops and the bare soil site-year). The 95% CI is provided for each model across a range of N fertilizer rates (0–300 kg·ha^{-1}). The IPCC tier 1 95% CI is 0.3–3%. The Philibert et al. (31) 95% CI encompasses parameter uncertainty.

approved methodologies at the American Carbon Registry (27) and Verified Carbon Standard (32): $Emis = [6.7(e^{0.0067}\ N - 1)]/N$, where N is N input in kilograms per hectare and *Emis* is N_2O emissions in grams of N_2O-N per hectare, with the best quadratic approximation of $Emis = (4.00 + 0.026\ N)N$. Using nontransformed emissions, Hoben et al.'s model (15) takes the form $Emis = (4.36 + 0.025\ N)N$. The model for upland grain crops in our study (Table S3) is similar but slightly less nonlinear: $Emis = (6.49 + 0.0187\ N)N$. In other words, the model from Hoben et al. (15) predicts somewhat lower emissions than the model derived for the average of upland grain crop experiments in our study for N inputs below 325 kg·ha^{-1}. We also obtained a very similar model for all crops when N-fixing crops were excluded: $Emis = (6.58 + 0.0181\ N)N$.

The ΔEFs for perennial grass/forage crops, which are predominantly nonleguminous grasses in this analysis (Dataset S1), did not differ significantly from those for upland grain or other non–N-fixing crops (Fig. 2). This suggests that N_2O emissions from cellulosic biomass grown for biofuel feedstock will behave similar to other crops: Small fertilizer additions will little affect N_2O emissions, but fertilization at levels greater than crop need will have a disproportionate and increasingly negative impact on N_2O emissions, as documented in a recent multiple N-rate switchgrass (*Panicum virgatum*) experiment (33).

Regional budgets might be significantly altered by replacing the constant IPCC 1% EF with an N-rate–dependent EF. In particular, this change would likely lower emission estimates from regions predominantly fertilized at low N inputs while increasing emission estimates from highly fertilized areas. Using a constant EF may explain why regional bottom-up estimates of N_2O emissions are inconsistent with top-down estimates (18, 22, 23).

For example, estimates of absolute N_2O emission rates for moderately fertilized grain crops, (e.g., US midwestern corn fertilized at an N input of 150–200 kg·ha^{-1}) will not much depend on estimation method; the IPCC 1% EF model yields values close to those of our ΔEF model. At higher and lower rates, however, the differences become significant. For crops underfertilized at an N input of 50 kg·ha^{-1} for example, N_2O emissions will be overestimated by 25% (0.5 vs. 0.37 kg of N_2O-N per hectare for the IPCC 1% EF model vs. the ΔEF model), whereas for crops overfertilized at an N input of 300 kg·ha^{-1}, N_2O emissions will be underestimated by 20% (3.0 vs. 3.6 kg of N_2O-N per hectare), and the difference grows exponentially for still higher rates. Fertilization rates at an N input of 500 kg·ha^{-1} are common in China's North China Plain region, for example (34), for which the IPCC 1% EF model will underestimate emissions by >50% (5.0 vs. 7.9 kg of N_2O-N per hectare).

The difference in EF models becomes significant for even moderate N fertilizer rates when calculating the reduction of N_2O emissions due to lowered N fertilizer inputs. In Fig. 4*A*, we compare modeled estimates derived from measurements in the midwestern corn fields of Hoben et al. (15), from the IPCC 1% EF model, and from our ΔEF model for upland grain crops (including corn) for a reduction of 50 kg·ha^{-1} in N input at four baseline applications: 300, 200, 150, and 50 kg·ha^{-1} (Fig. 4*B*). For all 50 kg·ha^{-1} reduction scenarios, the IPCC-based emission reduction estimate is 0.5 kg of N_2O-N per hectare. When reducing from an N input of 300 to 250 kg·ha^{-1}, the IPCC-based estimate is 44% less than the 0.9 kg of N_2O-N per hectare reduction estimate for Hoben et al.'s model (15) and 40% less than the 0.84 kg of N_2O-N per hectare reduction estimate for our ΔEF model for upland grain crops. When reducing from an N input of 200 to 150 kg·ha^{-1}, the IPCC-based emission reduction estimate is 30% less than the estimate of 0.65 kg of N_2O-N per hectare for the other two models. In contrast, for a reduction from an N input of 150 to 100 kg·ha^{-1}, all three models had about the same emission reduction estimate (0.5–0.56 kg of N_2O-N per hectare). Conversely, for a reduction of N input from 50 kg·ha^{-1} to no fertilizer application, compared with the IPCC-based emission reduction estimate, the model of Hoben et al. (15) and the ΔEF upland grain crop model estimated reductions of only 0.28 and 0.37 kg of N_2O-N per hectare, respectively.

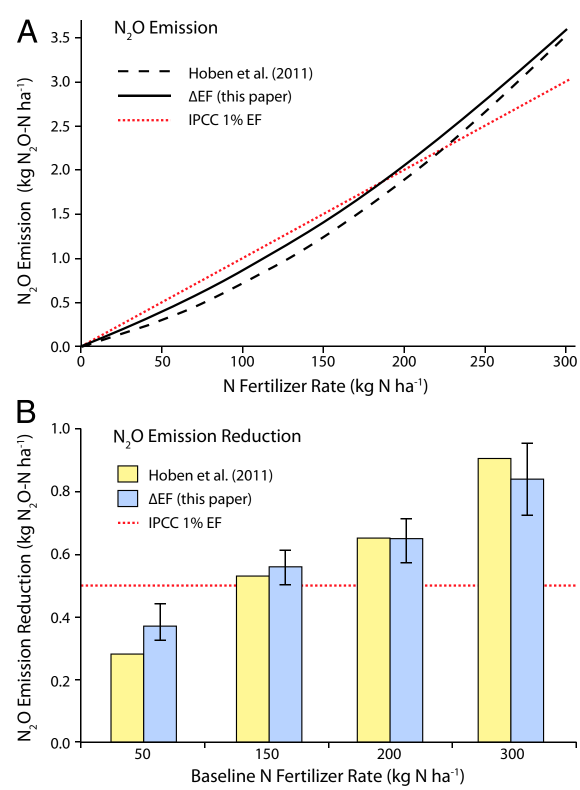

Fig. 4. (*A*) Comparison of N_2O emission models for N fertilizer reduction scenarios: N_2O emissions estimated by the IPCC tier 1 (1% linear emission: 0.01 N) model, the Hoben et al. (15) model (0.001 N[4.36 + 0.025 N]), and the ΔEF model for average upland grain crop emissions from this meta-analysis (0.001 N[6.49 + 0.0187 N]). (*B*) Relative N_2O emission reductions for the three models when N fertilizer rates are reduced by 50 kg·ha^{-1} from four baseline N fertilization scenarios: 300, 200, 150, and 50 kg·ha^{-1}. Vertical lines denote SEs for emission estimates based on the ΔEF model.

Thus, when models are used to estimate the impact of N fertilizer reductions on N_2O emissions (e.g., ref. 26), it will be especially important to avoid overestimating the impact of reductions where N is applied at rates close to crop N needs and, conversely, underestimating the impact of reductions where N is overapplied. This means that the largest mitigation gains are to be made where fertilizer N is applied in excess, such as in many areas of China, and little mitigation will be gained where fertilizer N is in greatest need, such as in many areas of Africa (34). Regional and global estimates of emissions are thus likely underestimating emission reductions due to lowered N application rates (see example above). This underestimation will not be balanced by overestimating reductions elsewhere, because economical N application reductions (with respect to yield) can only be made in fields where N is currently being applied in excess, so at higher N rates. Our ΔEF model predicts higher N_2O emission reductions than the IPCC tier 1 model for N applications above 90 $kg{\cdot}ha^{-1}$, covering most land in need of N-input reduction.

We believe our ΔEF model can be used as a more biologically appropriate value for estimating direct N_2O emissions from agricultural cropland than the current IPCC 1% default. The ΔEFs for particular crops and soil types where the dataset is sufficiently abundant can separately function as tier 2 ΔEFs for these particular conditions (Fig. 2). The use of one or more of these ΔEFs should improve the accuracy of national and regional inventories for direct N_2O emissions from fertilized agricultural land, especially where fertilizer rates are well outside the range of crop need (Fig. 4*A*), as noted above.

Nevertheless, at present, we do not believe there is sufficient evidence for using different ΔEFs for different crops or fertilizer types except for the exceptional case of fertilized legumes, which seem to have an extraordinarily high ΔEF. No nonleguminous crops in the analysis differ significantly from one another, however (Fig. 2*A*), and their emissions are best characterized by the formula $Emis = (6.58 + 0.0181\ N)N$, where N is input in kilograms of N per hectare, and *Emis* is grams of N_2O-N per hectare. Likewise, there seems little reason to differentiate among fertilizer types with the evidence available here. Although AN appears to have an extraordinarily high ΔEF, it does not differ significantly from that of urea nor synthetic fertilizers in general ($P > 0.05$) and the number of site-years available for comparisons ($n = 27$) is relatively low. Whereas some fertilizer types appear to have a ΔEF not different from zero, those cases tend to suffer from a low sample size, such as for CRU ($n = 6$). Likewise, the ΔEF for manure ($n = 16$) is not significantly different from zero but also is not significantly different from the ΔEF for synthetic fertilizers in general. Until more evidence is available, we believe the general formula given above is appropriate for all situations except N-fertilized legumes.

A significant shortcoming of this analysis is few site-years with four or more nonzero N-input levels. With a sufficient number of fully resolved N_2O response curves, we would be better able to generalize the shape of the ΔEF function with higher confidence. In fact, ΔEFs as calculated in this analysis are likely to be lower than those that will be generated from studies with additional N-input levels. This is because studies with few N-input levels are less likely to capture the precise inflection point where N_2O fluxes accelerate as crop N needs are met. Indeed, in some proportion of the studies in the present analysis, the first nonzero N-input level may already be above crop N needs, as suggested by ΔEFs that are substantially smaller for studies where the lowest nonzero N rates are >100 $kg{\cdot}ha^{-1}$ (Fig. 2*C*).

Thus, more studies with five or more input levels are needed, particularly for heavily fertilized crops such as maize and vegetables. Needed especially are additional studies in climate zones other than north temperate, in rice and upland grain crops, and with different fertilizer formulations and application timings. Further knowledge of the factors and practices that affect N_2O emissions from agricultural soils is crucial not only for developing effective mitigation strategies for this important GHG but also for developing a more robust means for balancing the global N_2O budget (18, 23, 35).

Methods

Study Selection and Data Extraction. We selected field studies from the literature where in situ measurements of at least three different levels of N input, including a zero N control, were applied under otherwise identical conditions, including site, growing season, crop, fertilizer type, measurement duration, frequency, and method (references in Tables S1–S9 and Dataset S1). We included in our search all published datasets from the Web of Science (selected from 1,330 papers found the using keywords "nitrous oxide fertilizer rate" in June 2013) and in studies identified in reviews by Bouwman (8), Jungkunst et al. (36), and Kim et al. (25). Laboratory and greenhouse studies were excluded from our analysis, as were studies where N inputs were confounded by differences in management practices.

We used all site-years present in the original studies, averaged by replicates (if reported). We did not average measurements for a particular site if years, crops, fertilizers, or other important factors were different. We converted units of fertilizer input, mean N_2O emission, and SE to kilograms of N per hectare for the study period.

Papers with data presented only as graphs of total or daily emissions were digitized using Get Data Graph Digitizer (37). Digitization errors were less than 1% in newer papers to ∼3–5% for old graphs with poor image quality or where daily emission values were used.

We include key characteristics for each study (Dataset S1) when available: literature reference; location name and coordinates of experiment; mean annual precipitation and temperature; soil texture, organic carbon, organic nitrogen, pH, and bulk density; selected crop and management details; year, duration, total number of measurements, and number of replicates; chamber area and number of samples per flux measurement; and fertilizer type, mode of application, and number of applications per measurement period (Table S2). Where necessary, we contacted corresponding authors to make this table as complete as possible.

ΔEFs. We calculated EFs for every nonzero N application rate (N) as a difference between N_2O emissions (ER_N) at the application rate and control (ER_0) divided by N: $EF_N = (ER_N - ER_0)/N$. The least squares linear relation between the EF and N application rate was found for each site-year [for those site-years with three N levels (two-point curves), the model had perfect agreement]: $EF_N = EF_0 + \Delta EF\ N$. The ΔEF (Fig. S5) of this relationship signifies the degree of nonlinearity of emission increase with N input: Zero ΔEF indicates that N_2O emissions grow linearly with N input (constant EF), a positive ΔEF indicates a faster than linear emission increase (increasing EF), and a negative ΔEF means that emissions grow at a rate slower than linear (decreasing EF). The model of linear change in EF assumes quadratic growth in emissions with N rate ($ER_N = ER_0 + [EF_0 + \Delta EF\ N]N$), but our goal was to analyze the nonlinear component (*ΔEF*; Dataset S1) and not to determine the specific shape of the response.

Data Analysis. Data analysis was performed using Mathematica (38). We performed a Kolmogorov–Smirnov test and determined that the distribution of ΔEF is not normal ($P < 0.0001$). We used nonparametric (resampling) and parametric procedures for further analysis. Resampling procedures [bootstrap (i.e., sampling with replacement of the size equal to the initial size of the subset repeated n = 100,000 times)] were used for analysis of means, medians, and CIs for all ΔEFs in the study, as well as subsets of ΔEFs and parametric statistics used to compare results.

We removed four outlier ΔEFs with the largest absolute values (−0.065, −0.05, 0.077, and 0.108) from further analysis because of their undue influence on subgroup means. The remaining 229 ΔEFs were divided into categories based on type of crop (N fixers, upland grain crops, rice, and perennial grass/forage), fertilizer type [AN, CAN, U (urea), M (manure), and Mixed] SOC content, soil pH (<7 and ≥7), mean annual precipitation, mean annual temperature, and lowest nonzero N-input level (0–100 and >100 $kg{\cdot}ha^{-1}$). Mean ΔEFs for subgroups were compared using a bootstrap test for differences (n = 100,000 between means obtained by sampling with replacement equal to the initial size of the subset) across the crop and fertilizer type groups for the same factor, with BH adjustment for the total number of tests to control the false discovery rate (28). We performed a linear regression analysis of ΔEF relative to mean EF.

We analyzed mean ΔEFs for potential biases due to sampling factors. We selected the value of a parameter that split the dataset into two categories of similar size. We repeated the above procedure for each of the following factors: number of fertilizer applications, total number of measurements, chamber area, number of samples per flux measurement, duration of the experiment, number of replicates, and number of input levels. We performed bootstrap tests for differences as above, but without adjustment for the total number of comparisons. In addition, we selected site-years with at least four N-input levels; we then fit a quadratic equation and divided that dataset into two categories of similar size by quality of the fit ($R^2 < 0.93$ and $R^2 \geq 0.93$) and tested the differences in ΔEFs.

We tested relatedness of pairs of different tested factors to each other to avoid relating the same influence to two different factors. For each pair of experimental and sampling factors, we calculated the phi-coefficient (ϕ), which is a measure of association of the two variables forming a two-by-two contingency table: $\phi = \sqrt{(\chi^2/n)}$, where χ^2 is derived from Pearson's χ^2 test and *n* is total number of observations (39).

Comparison with Previous Studies. We determined the best quadratic model for each individual site-year. We determined the mean quadratic model and used a resampling procedure to obtain the 95% CI for all of the site-years in our dataset, excluding sites with N-fixing crops and bare soil. We compared this CI with 95% CIs for IPCC tier 1 methodology and for the range of six models used by Philibert et al. (31), including and not including parameter uncertainty. Selecting only studies with four or more N-input levels in our dataset, we performed a procedure described by Kim et al. (25) to classify all site-years into categories of linear, faster than linear (exponential), and slower than linear (hyperbolic) N_2O emission increases with N input.

We determined a quadratic model for each site-year and then obtained an average model for each group of site-years in the form $Emis = (EF_0 + \Delta EF\ N)N$, where EF_0 is the EF at an N input of 0 kg·ha^{-1}, ΔEF is the EF change rate, *N* is N input in kilograms of N per hectare, and *Emis* is grams of N_2O-N per hectare (Table S3). We compared the mean quadratic model for upland grain crops ($Emis = [6.49 + 0.0187\ N]N$) with the model of Hoben et al. (15) based on untransformed emissions ($Emis = [4.36 + 0.025\ N]N$) and the IPCC 1% EF model ($Emis = 10N$). We estimated the differences in emissions reductions predicted by each model under reduction in N fertilizer input from 300 to 250 kg·ha^{-1}, from 200 to 150 kg·ha^{-1}, from 150 to 100 kg·ha^{-1}, and from 50 to 0 kg·ha^{-1}.

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