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A gap in nitrous oxide emission reporting complicates long-term climate mitigation

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Nitrous oxide (N_2O) is an important greenhouse gas (GHG) that also contributes to depletion of ozone in the stratosphere. Agricultural soils account for about 60% of anthropogenic N_2O emissions. Most national GHG reporting to the United Nations Framework Convention on Climate Change assumes nitrogen (N) additions drive emissions during the growing season, but soil freezing and thawing during spring is also an important driver in cold climates. We show that both atmospheric inversions and newly implemented bottom-up modeling approaches exhibit large N_2O pulses in the northcentral region of the United States during early spring and this increases annual N_2O emissions from croplands and grasslands reported in the national GHG inventory by 6 to 16%. Considering this, emission accounting in cold climate regions is very likely underestimated in most national reporting frameworks. Current commitments related to the Paris Agreement and COP26 emphasize reductions of carbon compounds. Assuming these targets are met, the importance of accurately accounting and mitigating N_2O increases once CO_2 and CH_4 are phased out. Hence, the N_2O emission underestimate introduces additional risks into meeting long-term climate goals.

N cycling | soil N_2O | GHG accounting | ecosystem modeling

Soil nitrous oxide (N_2O) emissions from agricultural management are a key source of greenhouse gas (GHG) emissions in many countries due to the widespread use of nitrogen fertilizers, manure amendments from livestock production, growing of legumes, and other practices that contribute nitrogen inputs to soils or alter the soil environment (1, 2). These emissions are quantified using two broad approaches: 1) top-down methods based on atmospheric N_2O concentration dynamics and inverse models, and 2) bottom-up methods based on soil-surface flux measurements combined with empirical and process-based models. Although top-down and bottom-up estimates of global N_2O emissions are consistent (3), uncertainty increases, and methods often diverge at smaller spatial scales and when emissions are partitioned into different source categories. For example, N_2O emissions estimated using top-down measurements were higher than those based on bottom-up approaches for the US Corn Belt (4, 5), an important agricultural region characterized by intensive cropping with substantial N inputs. In contrast, a study in Europe found that N_2O emissions inferred from inversions were consistent with those reported in national inventories based on bottom-up methods (6).

Nitrous oxide emissions are assumed to be primarily or entirely driven by N inputs based on bottom-up methods that use empirically derived emission factors at large spatial and temporal scales. However, N_2O is produced by various biochemical processes and N inputs interact with weather, soil properties, plant growth patterns, wet–dry/freeze–thaw cycles, microbial/enzymatic dynamics, and other factors to determine field-scale emissions, which often exhibit high spatial and temporal variability (7). Despite these complexities, the methods most commonly used to estimate emissions reported in national GHG inventories are based on emission factors developed by the Intergovernmental Panel on Climate Change (IPCC) that assume emissions are proportional to N inputs (8–10).

The United States is an exception in that the DayCent ecosystem model is used to estimate N_2O emissions from agricultural soils for national reporting (1). DayCent simulates the plant/soil system processes that cycle N and accounts for how management and environmental conditions influence emissions (7, 11). The model has been calibrated and evaluated with observational data across many research sites and has been shown to be more accurate than the IPCC emission factors (1). However, a gap potentially exists in reporting N_2O emissions with DayCent. Emissions are likely to be underestimated because the model does not reproduce the N_2O emission patterns associated with freeze–thaw cycles that have been observed in field studies and are responsible for a large proportion of the annual emissions in northern cold climate systems (12). Atmospheric inversion analyses have also found a regional pulse of emissions coinciding with the

Significance

Efforts to quantify greenhouse gas emission reductions needed to achieve climate targets such as those formulated in the Paris Agreement (and to share the efforts fairly among countries) need to be based on the best available science. We demonstrate that, for the United States, ecosystem models can account for soil, plant, and fertilization conditions to quantify the emissions of nitrous oxide (N_2O), and adequately cover observed large pulses due to soil freezing and thawing events. For national reports to the climate convention, most other countries rely on a simple linear approach. While sufficient to estimate CO_2 emissions, ongoing efforts to curb other important greenhouse gases and the need of agricultural intensification without extra emissions will require more accurate N_2O inventories.

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timing of the early spring thaw in parts of the northern United States (13). We have modified DayCent to represent freeze–thaw–induced N_2O emissions to evaluate the impact on national reporting of emissions and explore mitigation implications related to long-term climate goals.

Results

Modeling Spring-Thaw Emissions. Pulses of N_2O emissions associated with freezing and thawing are thought to result primarily from denitrification, an anaerobic process driven mainly by heterotrophic microbes that reduce nitrate (NO_3^-) to N_2O and other N species when O_2 is limiting (12). Two sites in Canada with high-quality N_2O flux data were chosen for initial DayCent testing of seasonal gas flux dynamics. Comparison of outputs from DayCent with micrometeorological N_2O flux data from agricultural research sites in Ontario and Manitoba showed that spring freeze–thaw–related emission pulses were significantly underestimated by more than a factor of 3 on average (*SI Appendix*, Fig. S1). DayCent assumes that N_2O emissions from denitrification are controlled by soil NO_3^- concentration, labile carbon (C) availability, water content, and soil properties that affect gas diffusion rates (14). Analysis of model outputs showed that limited labile C availability and simulated water contents that are too low to maintain anaerobic conditions typically prevented the observed early spring emission pulses in the model simulations.

The model has been adjusted to address this limitation to allow emission pulse events triggered by thawing with relaxed constraints on denitrification due to labile C and water content controls. This approach assumes that there is more heterogeneity in the soil surrounding the formation of anaerobic microsites as the soil thaws and refreezes and in the availability of C substrate than is represented by modeling bulk water content or soil C. In addition, the pulse magnitude and duration are proportional to winter-season cumulative freezing degree-days (CFDs), as shown by Wagner-Riddle et al. (12). Different spring freeze–thaw algorithms were parameterized using observations from research sites in Manitoba, Ontario, and Colorado (see *Methods* and *SI Appendix*, Table S1 for details). Graphical (*SI Appendix*, Figs. S1 and S2) and statistical (*SI Appendix*, Table S2) analyses showed clear evidence that including pulse events associated with thawing significantly improved model predictions compared with the original model structure. Freeze–thaw pulses in DayCent are triggered by thawing of the 2- to 5-cm soil layer based on model evaluation (*SI Appendix*, Table S2).

To investigate the importance of freeze–thaw–related N_2O emissions over a large land area, we compared DayCent predictions with regional-scale emissions from atmospheric inversions for the northcentral region of the United States (Fig. 1) (13). The enhancement of relaxed soil water content and labile C controls on denitrification during the spring freeze–thaw events predicts emissions that are more comparable to the atmospheric inversion analysis (*SI Appendix*, Table S2). Both the atmospheric inversion results and DayCent-modeled emissions showed prominent pulses during late winter and spring related to thawing, as well as subsequent pulses in early summer from fertilizer additions to soil, and DayCent almost always overlapped the uncertainty range of the inversions (Fig. 1). Although seasonal pulse timing was similar, pulse magnitude inferred from the inversions tended to be greater than DayCent and mean annual emissions from the inversions exceeded those from DayCent by about 73%. Emissions inferred from the inversions also exhibited more interannual variability than those from DayCent (coefficient of variation of 28 and 4% for inversions and DayCent, respectively). One challenge is that emissions from the inversions must be partitioned before being compared with DayCent emissions for agricultural soils. This is done based on assumptions, some of which are uncertain, such as N_2O emissions from aquatic systems within and surrounding farms. Which method is more accurate cannot presently be determined and future research should rigorously calculate and compare uncertainties in top-down and bottom-up approaches. Regardless, the pattern of spring-thaw emission pulses estimated with DayCent is consistent with atmospheric inversions, providing further evidence that the pulses are widespread in the region during the spring as the soil is thawing.

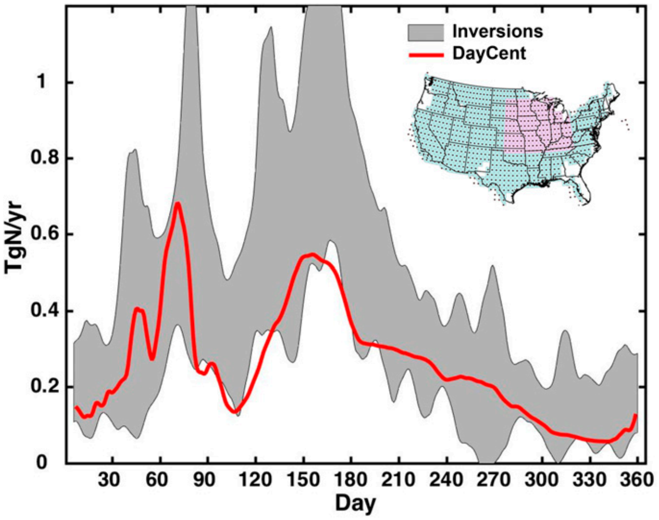

Fig. 1. N_2O emissions (seasonal means 2008 to 2012) from cropped and grazed soils in the northcentral region of the United States (*Inset*) comparing DayCent simulations with emission uncertainty bounds derived from atmospheric inversions.

Quantifying US Emissions. We assessed the impact of freeze–thaw events on GHG inventory reporting to the United Nations Framework Convention on Climate Change (UNFCCC) (15) for agricultural soil N_2O emissions across the United States from 1990 to 2015. DayCent is used to quantify N_2O emissions from most cropland and grassland soils reported in the national GHG inventory, compiled annually by the US Environmental Protection Agency (EPA) (1). Briefly, comprehensive databases for environmental (weather, soil type) and management practices (vegetation type, N fertilizer and water inputs, tillage intensity, cover crops, other management practices) are used to drive DayCent model simulations (see *Methods* for details). Simulations are conducted at a fine spatial resolution (about 340,000 parcels throughout the conterminous United States) using historical and contemporary land management, weather, and soil data (1). To investigate spatial patterns, we calculated the difference in mean annual emissions, [freeze–thaw–modeled emissions] − [no freeze–thaw–modeled emissions], at a fine spatial resolution (Fig. 2). The differences ranged from negligible to 0.7 kg N_2O-N·ha^{-1}·y^{-1} and were larger in colder regions that accumulated more freezing degree-days. As expected, the freeze–thaw enhancement had no impact in warm southern and West Coast regions where plant hardiness zones are 7 or greater with limited or no soil freezing during the winter.

While the accumulation of enough freezing degree-days is one of the requirements for DayCent to simulate the emission pulses from freeze–thaw events, on its own it is not enough to substantially increase emissions during the early spring period. For example, increases were not large in most of Wisconsin and

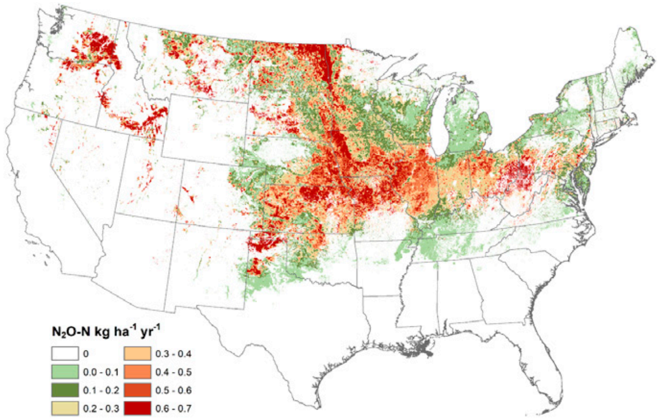

Fig. 2. Difference in DayCent-simulated N_2O emissions from cropped and grazed soils (1990 to 2015 mean) obtained by subtracting emissions from DayCent without freeze–thaw enhancement from DayCent with freeze–thaw dynamics.

Michigan (Fig. 2), where relatively low N inputs through fertilization limit the amount of residual nitrate in soil and constrain the magnitude of spring-thaw pulses. In contrast, Illinois had large spring N_2O pulses, as a large portion of agricultural land is managed with high fertilizer inputs for corn production and has a high prevalence of N-fixing legumes, namely soybeans. In addition to N availability, low water inputs likely limit emissions in parts of the northwestern region of the United States, where dryland cropping is a dominant land use. At the national scale, freeze–thaw events resulted in an average annual increase in emissions of 11%, which ranged from 6 to 16% across the time series from 1990 to 2015.

For national reporting to the UNFCCC, not accounting for spring thaw–induced emissions leads to an underestimation in N_2O emissions from cold climates, as found in northern regions of the United States, which would likely also be the case in many countries north or south of the respective subtropical zones, which can experience freeze–thaw cycles. The IPCC (8) prescribes a tiered system for GHG inventory reporting: tier 1 methods that use globally derived emission factors, tier 2 methods that use national or regional factors, and tier 3 methods that use observations or process-based models. To calculate emissions from cropland and grasslands, most nations use IPCC tier 1 methodology (8) that assumes 1% of N inputs from synthetic fertilizers, manure, and other organic amendments, along with unharvested residues, will be emitted as direct N_2O (i.e., N_2O emitted from the fields where N was applied), and 0.35% will be emitted as indirect N_2O (i.e., N_2O resulting from N transported from cropped/grazed fields via volatilization or nitrate leaching and converted to N_2O offsite). Because this method is driven entirely by N inputs and is mostly calibrated to N_2O observations from the growing season (16), it is likely that emissions are underestimated for some countries in cold climates. In fact, Wagner-Riddle et al. (12) estimated that global agricultural soil N_2O emissions were underestimated by 17 to 28% due to the omission of N_2O pulses from freeze–thaw events. DayCent had a lower spring thaw–induced emission gap of 6 to 16% compared with the Wagner-Riddle et al. (12) study because DayCent partially accounted for these emissions before developing the freeze–thaw enhancement. In particular, some of the datasets used for calibration had sufficient sampling during spring to allow for reliable quantification of cumulative annual emissions, which were used to calibrate the previous version of DayCent. However, modeled emissions in aggregate were biased toward underestimation because most published N_2O studies only report growing-season fluxes (17). In addition, the estimates from the study by Wagner-Riddle et al. (12) were based on CFDs alone, which, unlike DayCent, do not account for water and nitrite limitation associated with denitrification. These additional controls likely reduce DayCent-generated denitrification rates in some regions.

In contrast to default IPCC tier 1 emission factors, process-based models like DayCent and denitrification-decomposition (DNDC) (18) have the ability to reproduce observed nonlinear responses to N additions (e.g., ref. 19). Using models that reproduce responses such as freeze–thaw emission pulses would allow for countries to estimate these emissions or an empirical method could be applied that incorporates observations during freeze–thaw periods (12). For example, Canada uses adjusted factors to account for spring pulses when calculating emissions reported in the national inventory with a tier 2 method. The implication that higher tier methods produce less biased estimates is consistent with previous research, such as studies showing that process-based models tend to better match experimental plot-level observations from crop and grazing sites (e.g., refs. 20–22). Recently, Xu et al. (23) compared estimates derived from top-down and bottom-up approaches for North America with those reported in national inventories for the United States, Canada, and Mexico and concluded that tier 3 methods yield improved estimates.

Long-Term Climate Goals. The nationally determined contributions for GHG mitigation commitments associated with the Paris Agreement (UNFCCC 2015) emphasize reducing CO_2 emissions from fossil fuel combustion. In contrast to other economic sectors in which CO_2 dominates, CH_4 and N_2O are the major GHG sources from agriculture and their reduction is more important for meeting mitigation targets in the agricultural sector (24). The Global Methane Initiative (https://www.globalmethane.org/) announced at COP26 prioritizes CH_4 mitigation because this gas has a short atmospheric lifetime (∼12 y), so climate benefits manifest quickly. Nitrous oxide, in contrast, has a long atmospheric residence time (>100 y) and accurate quantification and mitigation of this gas increase in importance as CO_2 and CH_4 targets are realized and as the time horizon widens. Accurate N_2O accounting would also better inform Earth system models and reduce uncertainty in calculations of the remaining carbon budget (25), where current and future non–CO_2-forcing fractions are important input parameters.

National GHG inventories that do not include freeze–thaw–induced N_2O emissions lead to a gap in reporting and, in turn, a lower baseline for evaluating mitigation targets for N_2O emissions from some regions with cold climates. Higher baseline emissions that include spring-thaw pulses imply that mitigation must be more aggressive to accomplish long-term goals. Fortunately, there are opportunities to adopt N_2O mitigation technologies by applying recommended N management practices, providing additional benefits beyond GHG mitigation (26). For example, applying enhanced efficiency N fertilizers at recommended rates and accounting for spatial variability in soil properties decrease gaseous and soluble N losses (27, 28) and associated N cascade effects of reactive N pollution in the environment (29), while also maintaining or enhancing crop yields (30). Some practices can reduce freeze–thaw pulses, for example no-tillage and use of cover crops can reduce CFDs through snow trapping and associated soil insulation (31). However, incentives may be required to accomplish widespread adoption of enhanced efficiency fertilizers, variable application rates, and other recommended practices to compensate for higher costs than conventional management (e.g., ref. 32). Such incentives could be provided by both government programs and private sector ecosystem service markets (33).

The identified gap in the estimation of N_2O emissions associated with spring freeze–thaw also has implications for stratospheric ozone (O_3) recovery and how the social costs of N_2O are quantified (34). Because other O_3-depleting gases have largely been phased out, N_2O emissions are now the primary anthropogenic O_3-depleting substance (35). Despite this, N_2O is not currently included in the Montreal Protocol. A similar situation is likely to occur if CO_2 and CH_4 reduction goals are accomplished. Consequently, it is essential for governments in regions with cold temperate and boreal climates to consider using higher-tier methods that include the freeze–thaw N_2O emission pulses in their baseline emissions to secure both tropospheric O_3 and climate goals.

Methods

DayCent Model Overview. The DayCent biogeochemical model simulates plant–soil system C and N dynamics, soil water content and temperature, and other ecosystem variables (11). Key submodels include plant growth and senescence of biomass, decomposition of dead plant material and soil organic matter, mineralization of N, and N transformations that contribute to N_2O emissions. Model inputs are daily maximum/minimum air temperature and precipitation, surface soil texture class, soil hydraulic properties, vegetation type, and land management information (e.g., cultivation timing and intensity, timing and amount of fertilizer and organic matter amendments, and cover crops). Soil organic matter is simulated to a depth of 30 cm (36), while water, temperature, and mineral N are simulated throughout the soil profile. Soil organic matter is divided into three pools based on decomposability: active (turns over in months to years), slow (turns over in decades), and passive (turns over in centuries). Nitrification and denitrification, the primary processes leading to soil N_2O emissions, are controlled by soil mineral N levels, water, temperature, and labile C availability. The model has been tested using site-level observations from various studies worldwide and is currently used to estimate GHG emissions from cropland and grassland soils reported annually in the *Inventory of Greenhouse Gas Emissions and Sinks* (1).

Data Sources. N_2O observations from three research sites were used to parameterize the freeze–thaw dynamics in DayCent (*SI Appendix*, Table S1). Two of the sites measured emissions at half-hour intervals using micrometeorological methods, including a corn/soy/wheat cropping system in Elora, Ontario, and a wheat/barley system in Glenlea, Manitoba (37). The high-frequency measurements were integrated into daily flux rates to match the time step of DayCent. The third parameterization site was an irrigated corn system near Fort Collins, Colorado, where N_2O was measured one to three times per week using ground-based chambers (38).

Atmospheric Inversion Analysis. The CarbonTracker-Lagrange regional inversion framework is based on atmospheric N_2O data from about 40 sites, including flask, tower, and aircraft samples, from the National Oceanic and Atmospheric Administration (NOAA) Global Greenhouse Gas Reference Network (GGRN) (https://www.esrl.noaa.gov/gmd/ccgg/). The inversion uses the Bayesian methodology and algorithms described by Yadav and Michalak (39) to solve a cost function that scales a prior guess of N_2O flux to minimize the differences between available atmospheric N_2O observations and the prior flux convolved with an atmospheric transport matrix from Weather Research and Forecasting - Stochastic Time-Inverted Lagrangian Transport (WRF-STILT) (13). The inversion was run daily for each year from 2008 to 2014 over a North American domain extending from 10 to 80°N and 170 to 50°W.

Denitrification Submodule Overview, Freeze–Thaw Development, and Evaluation. Denitrification, the reduction of NO_3^- to nitrite (NO_2^-), nitric oxide (NO), N_2O, and dinitrogen (N_2), is controlled by soil NO_3^- concentration, labile C availability, water content, and soil properties that affect gas diffusion rates (14). Potential denitrification is down-regulated based on soil water content andsoil properties that influence gas diffusion rates and O_2 availability. Operationally, the model does not explicitly represent all the reduction steps and assumes that the law of the minimum applies in estimating the rate of nitrification (i.e., the most limiting resource or condition drives the rate on a given day). For example, the initial control on denitrification is typically either labile C (e— donor) or NO_3^- (e— acceptor) availability, whichever is more limiting. The initially calculated rate is down-regulated based on soil water content, texture, and CO_2 respiration rates which are combined and serve as a proxy for soil redox potential. The model then partitions N_2 and N_2O gases from denitrification using an N_2/N_2O ratio function which assumes that a higher portion will be in the form of N_2 gas as diffusivity decreases and as the ratio of e— donor to e— accepter increases.

The mechanisms responsible for freeze–thaw N_2O emission pulses are not entirely understood. The general hypotheses include accumulation of denitrification substrates while the soil is frozen that are suddenly released upon thawing; impacts on soil gas diffusivity and O_2 availability in pores during freeze–thaw events that influence denitrification rates; and differing temperature sensitivities of the enzymatic processes that control the amounts of N_2 and N_2O gases released during denitrification (40). Simplifications were made in model development (e.g., not accounting for local spatial heterogeneity of soil properties within fields and assuming they do not vary temporally; implicit rather than explicit representation of microbial dynamics) due to incomplete understanding of the processes involved, and so our approach to modeling freeze–thaw dynamics is semimechanistic. That is, we did not attempt to explicitly represent the mechanisms listed above (e.g., freeze–thaw impacts on labile C availability and gas diffusion rates). Instead, we used proxy relationships to model these impacts that included relaxing water constraints and releasing carbon controls on denitrification. In DayCent, bulk soil water-filled pore space (WFPS), modified by a gas diffusivity index, is a proxy for anaerobic volume where denitrification may occur. This constraint was relaxed by shifting the inflection point of the WFPS arctangent function to allow denitrification to occur at lower water contents due to the likelihood of anaerobic microsites forming in the soil as freezing and thawing occurs, which is not captured by modeling bulk WFPS. Similar to WFPS, simulated heterotrophic respiration rates are used as a proxy for labile C availability. The labile C constraint was eliminated by temporarily removing this control from the denitrification equation due to enhanced availability of labile C under freeze–thaw conditions following winter that is not captured with bulk respiration in DayCent. Eliminating this constraint does not impact C flows because modeled respiration rates are not explicitly enhanced. In contrast to C flows, N gas losses from freeze–thaw–enhanced denitrification rates do deplete the soil nitrate pool.

We considered seven representations of freeze–thaw–induced emissions, including pulses triggered by melting of snow or water in the 0- to 2- or 2- to 5-cm soil layer, minimum CFDs required to initiate a pulse, maximum CFD above which further accumulation does not enhance pulse magnitude and duration, if CFDs are reset to 0 after a pulse, and if labile C, soil water content, or both constraints should be relaxed during the pulse episode (*SI Appendix*, Table S2). Equation parameters in the different representations were optimized using a grid-based search and observations from the research sites described above (*SI Appendix*, Table S1). Evidence was mixed, but generally, algorithms based on snow melting had lower rms error, while those triggered by soil thawing had lower bias (*SI Appendix*, Table S2).

To further evaluate the different freeze–thaw representations, we compared them with regional-scale emissions for the US northern Great Plains and Corn Belt regions estimated using atmospheric inversions (Fig. 1). Five years (2008 to 2012) of soil N_2O flux data inferred from inversions were available (13). We used model architecture and input files for the national GHG inventory to generate DayCent N_2O for the region (1). Simulations were conducted without spring-thaw enhancement and three representations (one triggered by soil thawing and two by snow melting) were compared with emissions inferred from the atmospheric inversions. In this case, the model that relaxed the soil water content and eliminated the labile C controls on denitrification for approximately 3 d upon melting of the 2- to 5-cm soil layer and increased pulse magnitude by an amount proportional to CFDs during the preceding winter season exhibited superior performance (*SI Appendix*, Table S2). Consequently, this representation was selected for national-scale simulations for this study's assessment and for GHG emission inventory reporting (1).

Our implementation is based on pulse timing that is controlled by soil thawing and magnitude by CFDs of the 2- to 5-cm soil layer. It is not entirely clear why CFD is correlated with freeze–thaw pulse magnitude. However, CFD likely integrates various controls such as the mineralization of organic matter and the associated accumulation of mineral N that can occur under frozen temperatures and the buildup of N_2O entrapped under frozen layers, which is suddenly released upon thaw (7). The temperature of depth-based soil layers is routinely represented in ecosystem models, so this enhancement did not increase model input burden. The use of CFD to control pulse magnitude, along with modifying the WFPS relationship and labile C constraint on denitrification, allowed us to improve model performance without explicitly representing the mechanisms involved and minimized added complexity. In contrast to more complex models, DayCent does not explicitly represent microbial community dynamics involved in processes such as denitrification. In addition, local spatial and temporal soil heterogeneity are not represented even though there is evidence that denitrification occurs in microsites where O_2 is depleted, and explicit representation of the soil matrix and interactions with denitrifier activity may improve model predictions (41). The disadvantage is that explicit representation of mechanisms increases input burden and there is no guarantee that model behavior improves. Optimal model complexity remains an open question (7) and efforts to evaluate the impacts of more explicit mechanisms are underway, such as microbial dynamics in DayCent (42).

Although including spring-thaw enhancement in the DayCent model increased model accuracy, uncertainties and limitations remain. Compared with atmospheric inversions, DayCent-derived N_2O emissions were lower and exhibited less interannual variability (mean 468 and 271 Gg N and coefficient of variation 28 and 4% for inversions and DayCent, respectively). We speculate that variability is lower for DayCent because emissions are strongly driven by N inputs that do not appreciably vary from year to year. In contrast, emissions derived from inversions may be more sensitive to annual weather patterns as well as to interannual variability in atmospheric N_2O sampling coverage. Another limitation is that we only considered direct soil N_2O emissions. Some excess N, mainly as NO_3^-, is leached or lost in surface runoff from the soil into groundwater/streams and converted to N_2O during aquatic denitrification. A portion of soil N is also volatilized to N-based gases deposited elsewhere and converted to N_2O. These offsite sources of N_2O are termed indirect emissions and contribute about one-fourth of total agricultural soil emissions in the United States (1). These emissions were removed from the top down–derived emissions, but they are highly uncertain.

National-Scale Simulations. DayCent was applied to estimate direct soil N_2O emissions representing most (∼85%) of the cropland and grassland area in the conterminous United States that has nonfederal ownership. DayCent simulations were conducted using the crop and land-use histories for survey locations in the National Resources Inventory (NRI) (43). The NRI is a statistically based sample of all nonfederal land and includes 349,464 survey points in agricultural land for the conterminous United States. Each survey point is associated with an expansion factor that allows scaling of N_2O emissions from NRI survey locations to the entire country. Daily maximum/minimum temperature and precipitation data are based on gridded weather data from the PRISM Climate Data product (44). Soil texture data were derived from the Soil Survey Geographic Database (SSURGO) (45). Other soil characteristics needed for simulations, such as field capacity and wilting-point water contents, were estimated from soil texture using a standardized hydraulic properties calculator (46). DayCent simulations assumed intensive tillage management, gradual improvement of cultivars, and gradual increases in fertilizer application from 1950 until 1978. Starting in the early 1980s, the simulations captured increased adoption of reduced-tillage and no-tillage management, enrollment in the Conservation Reserve Program (a federal program that allows land to be set aside from production), along with cover crop adoption in the 2000s. Manure amendments also vary over the simulations based on livestock population data and availability of manure N for application to soils. Realistic simulations of historical land management and vegetation types are important because they influence present-day soil carbon and nitrogen levels, influencing N_2O emissions. The simulation methods can be found in the *Inventory of Greenhouse Gas Emissions and Sinks* (1).

Data Availability. DayCent model results are reported in US EPA (1). Temporally resolved DayCent N_2O outputs and inversion data are archived at Mountain Scholar (http://dx.doi.org/10.25675/10217/235393) (47). Site-level N_2O data are published in citations in *SI Appendix*, Table S1 and are available at https://dataverse.scholarsportal.info/dataverse/ugadr/?q=wagner-riddle (Ontario) and https://usdaars.maps.arcgis.com/apps/MapSeries/index.html?appid=9415d09247f64ae5bde462a3a9292e6c (Colorado).

Model result data reported in this article have been deposited at http://dx.doi.org/10.25675/10217/235393. Previously published data were used for this work (1, 13, 31, 37).

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1. US Environmental Protection Agency (US EPA), *Inventory of Greenhouse Gas Emissions and Sinks: 1990–2019* (430-R-21-005, EPA, 2021).
2. K. A. Smith, Changing views of nitrous oxide emissions from agricultural soil: Key controlling processes and assessment at different spatial scales. *Eur. J. Soil Sci.* **68**, 137–155 (2017).
3. H. Tian *et al.*, A comprehensive quantification of global nitrous oxide sources and sinks. *Nature* **586**, 248–256 (2020).
4. Z. Chen *et al.*, Partitioning N_2O emissions within the US Corn Belt using an inverse modeling approach. *Global Biogeochem. Cycles* **30**, 1192–1205 (2016).
5. M. Eckl *et al.*, Quantifying nitrous oxide emissions in the U.S. Midwest: A top-down study using high resolution airborne in-situ observations. *Geophys. Res. Lett.* **48**, e2020GL091266 (2021).
6. P. Bergamaschi *et al.*, Top-down estimates of European CH_4 and N_2O emissions based on four different inverse models. *Atmos. Chem. Phys.* **15**, 715–736 (2015).
7. S. J. Del Grosso *et al.*, Approaches and concepts of modelling denitrification: Increased process understanding using observational data can reduce uncertainties. *Curr. Opin. Environ. Sustain.* **47**, 7–45 (2020).
8. C. de Klein *et al.*, "N_2O emissions from managed soil, and CO_2 emissions from lime and urea application" in *2006 IPCC Guidelines for National Greenhouse Gas Inventories, Vol. 4: Agriculture, Forestry and Other Land Use*, S. Eggleston, L. Buendia, K. Miwa, T. Ngara, K. Tanabe, Eds. (IGES, Kanagawa, Japan, 2006), pp. 11.1–11.54.
9. K. Hergoualc'h *et al.*, "N_2O emissions from managed soils, and CO_2 emissions from lime and urea applications" in *Refinement to the 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Vol. IV*, C. Buendia *et al.*, Eds. (IPCC, Geneva, Switzerland, 2019), pp. 11.1–11.48.
10. S. M. Ogle, K. Butterbach-Bahl, L. Cardenas, U. Skiba, C. Scheer, From research to policy: Optimizing the design of a national monitoring system to mitigate soil nitrous oxide emissions. *Curr. Opin. Environ. Sustain.* **47**, 28–36 (2020).
11. W. Parton *et al.*, "Five decades of modeling supporting the systems ecology paradigm" in *Natural Resource Management Reimagined: Using the Systems Ecology Paradigm*, R. Woodmansee, J. Moore, D. Ojima, L. Richards, Eds. (Ecology, Biodiversity and Conservation 90-130, Cambridge University Press, Cambridge, UK, 2021), pp. 90–130.
12. C. Wagner-Riddle *et al.*, Globally important nitrous oxide emissions from croplands induced by freeze–thaw cycles. *Nat. Geosci.* **10**, 279 (2017).
13. C. Nevison *et al.*, Nitrous oxide emissions estimated with the CarbonTracker-Lagrange North American regional inversion framework. *Global Biogeochem. Cycles* **32**, 463–485 (2018).
14. S. J. Del Grosso *et al.*, General model for N_2O and N_2 gas emissions from soils. *Global Biogeochem. Cycles* **14**, 1045–1060 (2000).
15. United Nations Framework Convention on Climate Change (UNFCCC), "Adoption of the Paris Agreement" (FCCC/CP/2015/L.9/Rev.1, United Nations Framework Convention on Climate Change, 2015).
16. A. F. Bouwman, L. J. M. Boumans, N. H. Batjes, Modeling global annual N_2O and NO emissions from fertilized fields. *Global Biogeochem. Cycles* **16**, 28–1–28-9 (2002).
17. Z. Shang *et al.*, Measurement of N_2O emissions over the whole year is necessary for estimating reliable emission factors. *Environ. Pollut.* **259**, 113864 (2020).
18. K. A. Kariyapperuma, C. Wagner-Riddle, A. C. Furon, C. Li, Assessing spring thaw nitrous oxide fluxes simulated by the DNDC model for agricultural soils. *Soil Sci. Soc. Am. J.* **75**, 678–690 (2011).
19. R. L. Thompson *et al.*, Acceleration of global N_2O emissions seen from two decades of atmospheric inversion. *Nat. Clim. Chang.* **9**, 993–998 (2019).
20. Q. Yue *et al.*, Evaluation of four modelling approaches to estimate nitrous oxide emissions in China's cropland. *Sci. Total Environ.* **652**, 1279–1289 (2019).
21. P. Goglio *et al.*, A comparison of methods to quantify greenhouse gas emissions of cropping systems in LCA. *J. Clean. Prod.* **172**, 4010–4017 (2018).
22. N. Fitton *et al.*, The challenge of modelling nitrogen management at the field scale: Simulation and sensitivity analysis of N_2O fluxes across nine experimental sites using DailyDayCent. *Environ. Res. Lett.* **9**, 095003 (2014).

23. R. Xu *et al.*, Magnitude and uncertainty of nitrous oxide emissions from North America based on bottom-up and top-down approaches: Informing future research and national inventories. *Geophys. Res. Lett.* **48**, e2021GL095264 (2021).
24. M. A. Clark *et al.*, Global food system emissions could preclude achieving the 1.5° and 2°C climate change targets. *Science* **370**, 705–708 (2020).
25. H. D. Matthews *et al.*, An integrated approach to quantifying uncertainties in the remaining carbon budget. *Commun. Earth Environ.* **2**, 7 (2021).
26. D. R. Kanter, S. M. Ogle, W. Winiwarter, Building on Paris: Integrating nitrous oxide mitigation into future climate policy. *Curr. Opin. Environ. Sustain.* **47**, 7–12 (2020).
27. D. L. Northrup, B. Basso, M. Q. Wang, C. L. S. Morgan, P. N. Benfey, Novel technologies for emission reduction complement conservation agriculture to achieve negative emissions from row-crop production. *Proc. Natl. Acad. Sci. U.S.A.* **118**, e2022666118 (2021).
28. L. Zhang *et al.*, Integrated assessment of agronomic, environmental and ecosystem economic benefits of blending use of controlled-release and common urea in wheat production. *J. Clean. Prod.* **287**, 125572 (2021).
29. J. N. Galloway *et al.*, The nitrogen cascade. *Bioscience* **53**, 341–356 (2003).
30. T. M. Maaz *et al.*, Meta-analysis of yield and nitrous oxide outcomes for nitrogen management in agriculture. *Glob. Change Biol.* **27**, 2343–2360 (2021).
31. C. Wagner-Riddle *et al.*, Intensive measurement of nitrous oxide emissions from a corn–soybean–wheat rotation under two contrasting management systems over 5 years. *Glob. Change Biol.* **13**, 1722–1736 (2007).
32. A. De Laporte *et al.*, Economic and environmental consequences of nitrogen application rates, timing and methods on corn in Ontario. *Agric. Syst.* **188**, 103018 (2021).
33. S. Wallander, D. Hellerstein, M. Bowman, "A history of economic research on soil conservation incentives" in *Soil and Water Conservation: A Celebration of 75 Years*, J. A. Delgado, C. J. Gantzer, G. F. Sassenrath, Eds. (Soil and Water Conservation Society, Ankeny, IA, 2020), pp. 57–69.
34. D. R. Kanter *et al.*, Improving the social cost of nitrous oxide. *Nat. Clim. Chang.* **11**, 1008–1010 (2021).
35. S. Solomon, Risks to the stratospheric ozone shield in the Anthropocene. *Ambio* **50**, 44–48 (2021).
36. R. B. Gurung, S. M. Ogle, F. J. Breidt, S. A. Williams, W. J. Parton, Bayesian calibration of the DayCent ecosystem model to simulate soil organic carbon dynamics and reduce model uncertainty. *Geoderma* **376**, 114529 (2020).
37. M. Tenuta, B. Amiro, X. Gao, C. Wagner-Riddle, M. Gervais, Agricultural management practices and environmental drivers of nitrous oxide emissions over a decade for an annual and an annual-perennial crop rotation. *Agric. For. Meteorol.* **276**, 107636 (2019).
38. A. R. Mosier, A. D. Halvorson, C. A. Reule, X. J. Liu, Net global warming potential and greenhouse gas intensity in irrigated cropping systems in northeastern Colorado. *J. Environ. Qual.* **35**, 1584–1598 (2006).
39. V. Yadav, A. M. Michalak, Improving computational efficiency in large linear inverse problems. *Geosci. Model Dev.* **6**, 583–590 (2013).
40. K. A. Congreves, C. Wagner-Riddle, B. C. Si, T. J. Clough, Nitrous oxide emissions and biogeochemical responses to soil freezing-thawing and drying-wetting. *Soil Biol. Biochem.* **117**, 5–15 (2018).
41. S. Schlute, J. Zawallich, H. J. Vogel, P. Dorsch, Physical constraints for respiration in microbial hotspots in soil and their importance for denitrification. *Biogeosciences* **16**, 3665–3678 (2019).
42. D. Berardi *et al.*, 21st-century biogeochemical modeling: Challenges for century-based models and where do we go from here? *Glob. Change Biol. Bioenergy* **12**, 774–788 (2020).
43. Natural Resources Conservation Service, USDA, *Summary Report: 2015 National Resources Inventory* (Center for Survey Statistics and Methodology, Iowa State University, Ames, IA, 2018).
44. PRISM Climate Group, PRISM Climate Data (Oregon State University, 2018). prism.oregonstate.edu. Accessed 18 July 2018.
45. Soil Survey Staff, Gridded Soil Survey Geographic (gSSURGO), Database for the Conterminous United States (Natural Resources Conservation Service, USDA, FY2019 Official Release, 2019). https://gdg.sc.egov.usda.gov/.
46. K. E. Saxton, W. J. Rawls, J. S. Romberger, R. I. Papendick, Estimating generalized soil-water characteristics from texture. *Soil Sci. Soc. Am. J.* **50**, 1031–1036 (1986).
47. S. M. Ogle, S. Del Grosso, C. Nevison, Nitrous oxide emissions from 2008 to 2012 for agricultural lands in the contermious United States. Mountain Scholar. http://dx.doi.org/10.25675/10217/235393. Deposited 17 May 2022.