

ARTICLE

Soil Fertility & Crop Nutrition

Modeling the contributions of nitrogen mineralization to yield of corn

Charles M. White¹  | Denise M. Finney²  | Armen R. Kemanian¹ | Jason P. Kaye³

¹ Dep. of Plant Science, The Pennsylvania State Univ., 116 Agricultural Sciences and Industries Building, University Park, PA 16802, USA

² Dep. of Biology, Ursinus College, 112 Thomas Hall, Collegeville, PA 19426, USA

³ Dep. of Ecosystem Science and Management, The Pennsylvania State Univ., 116 Agricultural Sciences and Industries Building, University Park, PA 16802, USA

Correspondence

Charles M. White, Dep. of Plant Science, The Pennsylvania State Univ., 116 Agricultural Sciences and Industries Building, University Park, PA, 16802.
Email: cmw29@psu.edu

Funding information

Northeast SARE, Grant/Award Numbers: GNE11-017, ONE17-306, SNE14-11; National Institute of Food and Agriculture, Grant/Award Numbers: 2011-51300-30638, 2013-67019-21369, 2015-51300-24156

Abstract

Nitrogen (N) mineralized from soil organic matter (SOM) and crop residues is an important source of N to crop nutrition but historically has been difficult to account for in N fertilizer recommendation systems. Here we propose and test relatively simple biogeochemical models that predict the contribution of N mineralization in supporting the yield of corn (*Zea mays* L.). The models are specifically designed to use soil and cover crop measurements that are easily accessible to farmers and agronomists, including soil carbon (C) concentration, 24-h CO₂ respiration of a dried and rewetted soil sample, soil texture, and cover crop biomass N content and C/N ratio. We calibrated the models to explain variation of and predict unfertilized corn yield using a dataset of 73 observations compiled from nine experiments conducted in different sites and growing seasons in Pennsylvania. A model using soil C to calculate contributions of SOM mineralization to N supply predicted unfertilized corn yields more accurately than a model using the 24-h CO₂ respiration ($r^2 = .62$ vs. $.47$; RMSE = 1.58 vs. 1.87 Mg ha⁻¹, respectively). Soil sand content played an important role in the models by regulating the humification efficiency, a term that partitions decomposing C and N between microbially assimilated and mineralized pools. These models are prototypes for a new generation of N decision support tools that answer many of the shortcomings of current N fertilizer recommendation systems and offer a novel step forward in N fertility management.

1 | INTRODUCTION

Nitrogen (N) mineralization is a critical ecosystem process supporting plant nutrition and crop yields in agricultural systems. Because N mineralization is regulated by a variety of ecological factors (Manzoni & Porporato, 2009), predicting N available to crops from mineralization can be difficult. As a result, crop N nutrition is often managed with over-abundant applications of mineral N fertilizer, which can lead to low

N use efficiency of fertilizers and N pollution in the environment (Robertson & Vitousek, 2009). Significant efforts to develop laboratory methods that predict N mineralization and are suitable for routine soil testing have been made (Bremner, 1965; Curtin et al., 2017; Fox, Roth, Iversen, & Piekielek, 1989; Franzluebbers, 2016; Khan, Mulvaney, & Hoeft, 2001; Schomberg et al., 2009). Although these efforts have yielded progress, a scarcity of field calibration to crop yields or the use of statistical and interpretation models (e.g., linear regression, Cate–Nelson plots) that do not represent the underlying ecosystem processes regulating N mineralization are shortcomings.

Abbreviations: PSNT, pre-sidedress soil nitrate test; SOM, soil organic matter.

This is an open access article under the terms of the [Creative Commons Attribution-NonCommercial-NoDerivs](https://creativecommons.org/licenses/by-nc-nd/4.0/) License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

© 2020 The Authors. *Agronomy Journal* published by Wiley Periodicals LLC on behalf of American Society of Agronomy

As early as the mid-twentieth century, the importance of the N mineralization process in supporting the N nutrition of crops was well recognized and a subject of significant research. Bremner (1965) summarized the early research on development of various N mineralization indices, which included chemical measures of soil organic N and carbon (C), laboratory incubations to measure mineralizable N, and microbial respiration assays. Although this line of research has continued through the current era (see references in previous paragraph), the practice of adjusting N fertilizer recommendations based on predictions of N mineralization is currently limited (Morris et al., 2018). However, the pre-sidedress soil nitrate test (PSNT) is one tool for adjusting N fertilizer recommendations using an in-season, field-based estimate of N mineralization that has been well developed and is widely supported (Fox et al., 1989; Magdoff, Ross, & Amadon, 1984). To our knowledge, PSNT interpretations and recommendations have not been calibrated to account for the unique patterns of N mineralization and resulting changes in N availability caused by different cover crop types (Kaye et al., 2019), however. Furthermore, using PSNT-derived recommendations also requires the ability to sidedress N fertilizer, which is not always an available management option.

Others have predicted cover crop residue N mineralization using computer simulations of the N cycle (Gaskin, Cabrera, Kissel, & Hitchcock, 2020; Melkonian, Poffenbarger, Mirsky, Ryan, & Moebius-Clune, 2017; Woodruff et al., 2018), which represents an important advance toward incorporating the mechanistic processes of N mineralization into agronomic decision making. However, these simulation models require the maintenance of a significant digital infrastructure such as computer servers, an online user interface, storage of user data, and procurement and assimilation of real-time weather data, which comes at an expense to the hosting organization and users. Furthermore, the model proposed by Woodruff et al. (2018) does not account for soil organic matter (SOM) mineralization, so although it can help determine the N fertilizer equivalence of cover crops, it provides limited utility in determining the overall N fertilizer requirement for a crop. Finally, computer simulation models that predict the pool of mineralized N from organic sources during the growing season have been criticized for their reliance on the mass balance approach to N fertilizer recommendations, where the mineralized pool of N substitutes proportionally for fertilizer in fulfilling the total crop N requirement determined from a yield goal (Rodriguez, Bullock, & Boerngen, 2019).

To address the limitations in current N decision support tools, here we develop an approach to predict N availability to corn from mineralization of SOM and cover crop residues using soil and plant tissue tests suitable for routine use in commercial testing laboratories and a mathematical model rooted in biogeochemical theory that is calibrated to crop yields measured in field experiments. Our approach is based

Core Ideas

- Biogeochemical equations of N mineralization predict the yield of unfertilized corn.
- The equations use routine plant and soil measurements to facilitate adoption.
- The equations could be used to improve N fertilizer recommendations.

on the assumption that N availability is a primary limiting factor in the yields of unfertilized corn; hence, the yield of unfertilized corn will respond proportionally to N mineralization from SOM and cover crop residues. In previous work (White, Finney, Kemanian, & Kaye, 2016), we used this assumption to calibrate a model to predict the effect of N mineralization from cover crop residues on the unfertilized yield of a subsequent corn crop (Equation 1):

$$\Delta Y = \alpha N_{cc} \left(1 - \frac{\varepsilon (C/N)_{cc}}{(C/N)_m} \right) \quad (1)$$

In this model, ΔY (Mg ha⁻¹) is the yield difference between corn in a plot with cover crop and an adjacent one without a cover crop. The N mineralization is regulated by the mass of N in cover crop residues (N_{cc} in kg ha⁻¹), the C humification efficiency (ε in g C g⁻¹ C), and the C/N ratio of cover crop residues and microbial biomass [$(C/N)_{cc}$ and $(C/N)_m$, respectively, in g C g⁻¹ N]. The humification parameter ε represents the proportion of decomposed C from cover crops that remains in microbial biomass or in stabilized soil C pools within the duration of N uptake by the subsequent cash crop. The parameter α is the grain yield response per unit of potentially mineralized N (Mg grain kg⁻¹ of N) and assimilates information about the environmental controls on decomposition rate and N use efficiency through regional calibrations to field data. A calibrated version of Equation 1 performed well at predicting the corn yield response due to cover crop N mineralization (White et al., 2016).

Predicting the yield difference relative to a non-cover-cropped plot has the advantage of controlling for the background N mineralization from SOM but poses a limitation to developing an overall N fertilizer recommendation for a field that accounts for both cover crop and SOM N mineralization. A method to account for the N supply from SOM and cover crops together, and thus predict the absolute yield of an unfertilized corn crop in a specific field, would make this approach more useful for managing N fertility.

Because N mineralized from SOM follows a similar biogeochemical pathway as N mineralized from cover crop residues, the formulation of Equation 1 could be adapted to include a component for organic matter N mineralization

using laboratory measures of SOM content, such as C or N concentration. Others have suggested that the respiration of CO₂ during a laboratory incubation of a dried and rewetted soil sample could be predictive of N mineralization in the field because of the stoichiometric coupling between C and N mineralization processes (Franzluebbers, 2016). Measurements of soil C concentration or CO₂ respiration could serve as the basis for alternative formulations of a mathematical model to predict N supply from SOM decomposition. Although these measures have long been known to relate to N mineralization (Bremner, 1965; Jenkinson, 1968), the relationships of soil C concentrations and laboratory CO₂ respiration with N mineralization are usually evaluated with linear statistical models (as in Schomberg et al., 2009) rather than a biogeochemical formulation of the N mineralization process.

In addition to temperature and moisture controls on the decomposition rate of cover crop residues and SOM, for which average regional conditions are accounted for in the calibration of α in Equation 1, some ecosystem models use soil mineralogy to regulate the C humification efficiency (Jenkinson, 1990; Parton, Schimel, Cole, & Ojima, 1987; Verberne, Hassink, De Willigen, Groot, & Van Veen, 1990). Carbon humification efficiency refers to the proportion of decomposing C that is assimilated into microbial biomass and stabilized soil C pools within a timeframe of interest (Kemanian & Stöckle, 2010; Mazzilli, Kemanian, Ernst, Jackson, & Piñeiro, 2015; White, Kemanian, & Kaye, 2014, 2016), which here is the period of growth and N uptake by a subsequent corn crop. This efficiency is related to the instantaneous C use efficiency of microbes (Sinsabaugh, Manzoni, Moorhead, & Richter, 2013) but also incorporates a temporal aspect, which recognizes that there may be multiple cycles of microbial predation on C substrates within the timeframe of interest (e.g., two cycles of microbial predation at a C use efficiency of 0.5 result in a net C humification efficiency of 0.25). The dependence of the C humification efficiency on soil mineralogy in many C and N cycling models arose from early experimental evidence of increased C and N mineralization rates in soils with greater sand-sized particle fractions (Sorensen, 1975, 1981) and gains further theoretical traction from more recent evidence demonstrating the role of organo-mineral surface interactions in protecting microbes and microbial byproducts from decomposition (Baldock & Skjemstad, 2000). Conceptually, soils with greater mineral surface area should have fewer cycles of microbial predation on organic substrates within a given time step, leading to a higher C humification efficiency (White et al., 2014). Adjusting the parameter ϵ in Equation 1 based on soil texture could improve our approach to predicting N supply from cover crops and SOM across a range of soil types.

Using results from distributed field experiments conducted across Pennsylvania, we tested the hypothesis that regionally calibrated, biogeochemically based models can explain the

yield of an unfertilized corn crop using laboratory measurements of soils and cover crops, including soil C concentration, CO₂ respiration, soil texture, cover crop N content, and cover crop C/N ratio. This novel approach addresses many of the limitations that have caused N decision support to be one of the largest uncertainties in agronomy. By processing data through a biogeochemical model rather than a conventional statistical model, we develop a decision support tool based on fundamental first principles that should be more robust and flexible in handling variations across site characteristics such as soil texture, SOM level, cover crop N content, and cover crop C/N ratio. We also account for multiple sources of organic N mineralization, both from cover crops and from SOM, which will be more useful in assessing overall contributions of N mineralization to the N fertility of a crop than to just determine a cover crop N fertilizer equivalence. Perhaps most importantly, by calibrating the model to ultimately predict corn yield rather than just a pool of mineralized N, we offer a solution to the criticism that mass balance–derived N fertility recommendations do not adequately account for the characteristics of the corn yield response to N additions (Morris et al., 2018; Rodriguez et al., 2019).

2 | MATERIALS AND METHODS

2.1 | Field experiments

A series of cover crop experiments were conducted in central and southeastern Pennsylvania from 2011 through 2014 in fields on commercial farms and at a university research station (Table 1). Corn growing season temperatures at the sites peaked in July, when mean monthly temperatures ranged from 22.5 to 25.3 °C (Table 2). Precipitation during the corn growing season was sufficient to realize normally expected yields at all sites, although monthly patterns of cumulative precipitation were highly variable within and across sites (Table 3). The minimum cumulative monthly rainfall across sites during the corn growing season was 28 mm, and the maximum was 199 mm. Soil taxonomic classes were Fine, mixed, semi-active, mesic Typic Hapludalfs at Experiments 1–5, 8, and 9 and Fine, illitic, mesic Typic Hapludalfs at Experiments 6 and 7.

Detailed field management at each of these experiments has been reported previously (Experiments 1–3 = Experiments 1–3 in White et al. [2016]; Experiments 4 and 5 in Finney, White, and Kaye [2016] and Experiments 6–9 = Montour (6 and 7) and Lancaster (8 and 9) locations in White et al. [2017]). Briefly, cover crop treatments (Table 4) were planted in late summer and terminated the following spring, and corn was planted in each field as the summer cash crop. Corn grain yields in unfertilized split-plots were then measured in the fall. Corn yields from cover cropped treatments in Experiments

TABLE 1 Experimental sites used in the model calibration, including number of observations, average soil pH (1:1 water), sand and clay, total soil C, CO₂ respiration, and unfertilized corn grain yield (dry basis) within each site

Experiment	Cover crop establishment year	Observations	Soil pH	Sand	Clay	Soil C	CO ₂ respiration	Unfertilized corn yield
		<i>n</i>			%		mg C kg ⁻¹ soil 24 h ⁻¹	Mg ha ⁻¹
1	2011	4	6.6	26	25	1.41	51.3	7.8
2	2012	3	7.1	20	55	1.30	78.6	2.9
3	2012	4	6.1	15	33	1.48	100.6	7.2
4	2012	3	6.1	15	33	1.31	40.8	7.0
5	2011	16	6.3	25	28	1.36	57.9	6.6
6	2012	10	6.7	18	21	1.27	76.3	5.8
7	2013	9	6.9	26	28	1.42	79.9	6.3
8	2012	12	7.0	29	23	1.90	106.3	10.0
9	2013	12	7.0	35	23	1.97	108.0	11.3

1–4 were previously used to calibrate a model to predict N supply from cover crop residues; therefore, only the no-cover-crop plots from these experiments are included in the analysis here. In Experiment 5, only no-cover-crop and monocultures of winterhardy grass and legume cover crop treatments were used in the current study in order to maintain a more balanced representation of experimental units from different sites. In Experiments 1–3, corn was planted with no-till soil and residue management, whereas soils were tilled to incorporate cover crop residues prior to corn planting in Experiments 4–9. Between-row cultivation with S-tine field cultivators was used to control weeds in the corn crop in Experiments 6–9, whereas Experiments 1–5 used residual herbicides to control weeds, and no further soil disturbance took place after corn planting.

2.2 | Field sampling and laboratory analyses

Cover crop biomass was sampled in fall at peak growth prior to winter senescence and in spring just prior to termination by cutting aboveground biomass from two 0.25-m² quadrats in each plot. The only cover crop species that winterkilled in any of the treatments was Austrian winter pea (*Pisum sativum* L. ssp. *sativum* var. *arvense*). Cover crop biomass was dried at 60 °C in a forced draft oven for approximately 2 wk, weighed, and ground to 1-mm fineness, and C and N concentrations were measured with a dry combustion elemental analyzer (EA 1110, CE Instruments). Soil samples were collected for total C and N and CO₂ respiration analysis during the corn phase of the experiment in June of each year. Six to eight soil cores (diameter, 1.8 cm; depth, 0–20 cm) were composited per plot. Soil samples were dried at 35 °C in a forced draft oven for approximately 2 wk. Samples were crushed and sieved by hand to 2-mm fineness for use in the CO₂ respiration analysis. Subsamples of soil used for total C and N analysis were

further pulverized with 5 min of shaking in a ball mill (8000D Mixer/Mill, Spex Sample Prep) and dried at 105 °C for 24 h prior to measuring total C and N concentration with a dry combustion elemental analyzer (EA 1110, CE Instruments). To measure soil texture, soil samples were composited by block of each experiment, and sand, silt, and clay fractions were determined by the hydrometer sedimentation method at the Penn State Agricultural Analytical Services Lab. Soil nitrate concentrations (0–20 cm depth) were measured in each experimental plot in spring just prior to cover crop termination as a reference point to document the inorganic N accumulated in the surface soil before corn planting. Soil sampling was conducted similarly to that described for the June sampling date. Fresh soil samples were kept in a cooler with ice prior to extraction to minimize nitrification. From each soil sample, a 10-g subsample of field moist soil was extracted in 100 ml of 2 M KCl within 3 h of sampling. Soil extracts were shaken for 1 h, filtered through Whatman #1 filter paper, and analyzed for NO₃[−]-N concentrations colorimetrically on a microplate spectrophotometer (Multiskan EX, Thermo Scientific) using the Griess reaction with vanadium(III) as a reducing agent (Doane & Horwáth, 2003).

Air-dried, 2-mm sieved soil samples were used to assess 24-h CO₂ respiration from rewetted soils using a protocol adapted from Franzluebbers, Haney, Honeycutt, Schomberg, and Hons (2000). The main adaptations were to use a 2-mm sieve size as opposed to a 4.75-mm sieve, to reduce the incubation time from 3 d to 24 h, and to measure CO₂ evolution in the headspace of sealed incubation jars with an infrared gas analyzer (LI-7100, LI-COR). The incubations were conducted by weighing 10 g of air-dry soil into a 50-ml plastic beaker, wetting the soil sample in the beaker to approximately 50% water-filled pore space with 3.1 ml of distilled water added by pipet to the top of the soil, and placing the soil beaker into a 464-ml glass jar sealed with a metal screw band lid (Ball Corporation) fitted with a rubber septum. The quantity of water needed to

TABLE 2 Monthly average air temperature during the corn production year in each experiment

Year	Experiments	Lat., long.	Jan.	Feb.	Mar.	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
°C (± SD)														
2012	1, 5	40.79, -77.87	-0.9 ± 4.7	1.6 ± 3.6	9.0 ± 3.6	9.4 ± 4.3	18.2 ± 3.6	20.0 ± 3.6	24.3 ± 3.7	24.3 ± 2.5	21.6 ± 2.5	17.0 ± 4.6	11.9 ± 4.5	2.5 ± 4.3
2013	2, 3, 4	40.79, -77.87	-1.4 ± 5.7	-2.6 ± 3.6	1.2 ± 3.3	9.8 ± 5.4	15.6 ± 5.0	20.7 ± 3.0	23.2 ± 3.0	20.6 ± 2.3	16.4 ± 4.3	12.3 ± 5.7	3.4 ± 5.6	-0.4 ± 5.7
2013	6	41.24, -76.92	-2.2 ± 4.9	-2.5 ± 3.0	1.8 ± 3.0	9.5 ± 5.0	15.2 ± 4.5	20.6 ± 2.8	23.7 ± 2.9	20.4 ± 2.2	16.3 ± 4.6	12.1 ± 5.4	3.2 ± 5.3	-1.1 ± 4.9
2014	7	41.24, -76.92	-7 ± 5.5	-5.5 ± 5.0	-0.8 ± 5.6	8.8 ± 4.3	15.3 ± 3.9	20.2 ± 2.6	21.4 ± 2.6	19.4 ± 1.9	17.2 ± 3.8	12 ± 3.3	2.8 ± 5.4	1.1 ± 2.8
2013	8	40.08, -76.07	1.2 ± 5.4	-0.1 ± 3.3	3.7 ± 2.7	11.5 ± 5.0	16.9 ± 5.1	22.4 ± 2.7	25.3 ± 2.9	22.3 ± 2.4	18.6 ± 4.1	14.3 ± 5.3	5.8 ± 5.2	1.9 ± 5.7
2014	9	40.08, -76.07	-3.8 ± 6.5	-2.2 ± 4.9	2.1 ± 5.4	10.6 ± 3.7	17.2 ± 3.4	22.2 ± 2.6	23.3 ± 2.5	22 ± 1.9	19.7 ± 3.7	14.2 ± 3.4	5.5 ± 5.4	3.1 ± 3.5

Note. Latitude and longitude coordinates are for the National Weather Service station closest to each site from which the records were accessed (Global Historical Climatology Network database, National Oceanic and Atmospheric Administration, U.S. Department of Commerce).

achieve approximately 50% water-filled pore space was determined by calculating the pore space of the sieved soil sample based on the bulk density realized when 40 g of sieved soil was added to the 50-ml plastic beaker and tapped once gently on the benchtop to simulate the settling that would occur from beaker handling during the procedure. Several replicate soil samples from each field site were tested in this manner, and a consistent bulk density was realized across all sites, justifying a standard water volume addition to every sample in the study. Sealed incubation jars were placed in a dark cabinet at 22 °C for 24 h. Headspace CO₂ concentrations after 24 h were measured from 1-ml gas samples removed through the rubber septa with a syringe and needle and injected into an infrared gas analyzer with a continuous flow of CO₂-scrubbed and dried carrier air. Concentrations of CO₂ were converted into mg C in the jar using the ideal gas law and the headspace volume, corrected for the mass of ambient CO₂ in the laboratory air measured in blank jars, and converted to mg C kg⁻¹ dry soil 24 h⁻¹ based on the mass of dry soil added to each incubation jar.

2.3 | Model specification

2.3.1 | N mineralization from SOM

Nitrogen mineralization from SOM is a biogeochemical process, with CO₂ respiration and soil organic C concentration measurements representing a flux and a pool size associated with the process, respectively. We therefore sought to identify biogeochemical equations that could serve as the basis for predicting N mineralization and N supply to corn from measurements of CO₂ respiration or soil C concentration. The classical biogeochemical equation for N mineralization is presented below (Manzoni & Porporato, 2009), where k_s is a decomposition rate of SOM, N_s is the N contained in SOM, ϵ is the C humification efficiency, C/N_s is the C/N ratio of SOM, and C/N_m is the C/N ratio of microbial biomass (Equation 2):

$$N_{\min} = k_s N_s \left(1 - \frac{\epsilon(C/N)_s}{(C/N)_m} \right) \quad (2)$$

To predict N mineralization from SOM, Equation 2 can be simplified and adapted to use inputs derived from routine soil testing practices. First, rather than using total N from soil, we used total C (C_s) as the input because it had a greater level of precision than the total N measurements. Although total C is not equivalent to organic C in all soils, in the humid-region soils of our study area the vast majority of total C is in the organic form. The only source of inorganic C in the <2 mm size fraction in these soils would be from recent limestone additions, and, even at the highest recommended limestone application rates, it would account for less than 1% of the total

TABLE 3 Monthly cumulative precipitation during the corn production year in each experiment

Year	Experiments	Lat., long.	Jan.	Feb.	Mar.	April	May	June	July	Aug.	Sept.	Oct.	Nov.	Dec.
mm														
2012	1, 5	40.79, -77.87	73	29	60	38	169	85	89	118	114	132	16	123
2013	2, 3, 4	40.79, -77.87	73	41	52	90	81	186	152	28	54	77	71	101
2013	6	41.24, -76.92	67	47	44	80	82	106	79	45	41	76	72	93
2014	7	41.24, -76.92	32	65	74	73	132	88	102	167	28	64	55	66
2013	8	40.08, -76.07	137	46	67	76	67	199	101	98	75	150	64	141
2014	9	40.08, -76.07	92	155	81	169	97	122	186	77	57	110	96	86

Note. Latitude and longitude coordinates are for the National Weather Service station closest to each site from which the records were accessed (Global Historical Climatology Network database, National Oceanic and Atmospheric Administration, U.S. Department of Commerce).

TABLE 4 Soil nitrate concentration (0–20 cm depth) measured in spring prior to cover crop termination and planting corn, winterkilled cover crop biomass N measured in fall at peak biomass, and winterhardy cover crop biomass N and C/N ratio measured in spring just prior to cover crop termination for each treatment within experiments

Experiment	Cover crop treatment ^a	Spring NO ₃ ⁻ -N mg kg ⁻¹	Cover crop biomass N		Winterhardy cover crop C/N g g ⁻¹
			Winterkilled	Winterhardy	
			kg ha ⁻¹		
1	No cover	2.8	–	–	–
2	No cover	0.9	–	–	–
3	No cover	3.7	–	–	–
4	No cover	6.3	–	–	–
5	No cover ^b	0.3	–	36	26
	HV	1.3	–	192	9
	RC	0.3	–	176	11
	RY	0.0	–	67	43
6	TR+AWP+CC	1.5	87	114	15
	CA+AWP+RY+RC	0.6	33	134	18
	RC	0.5	–	130	12
7	CA+AWP+RY+RC	2.0	7	81	15
	RC	4.7	–	67	10
	TR+AWP+CC	2.7	61	100	14
8	RC+LC+SC	0.5	–	88	13
	CA+AWP+RY+RC	0.4	5	132	15
	RC	1.0	–	74	9
9	RC+LC+SC	2.8	–	95	9
	CA+AWP+RY+RC	1.7	2	69	18
	RC	3.0	–	96	10

^aAWP, Austrian winter pea (*Pisum sativum* L. ssp. *sativum* var. *arvense*); CA, canola (*Brassica napus* L.); CC, crimson clover (*Trifolium incarnatum* L. 'Dixie'); HV, hairy vetch (*Vicia villosa* Roth); LC, ladino white clover (*Trifolium repens* L. 'Ladino'); RC, red clover (*Trifolium pratense* L.); RY, cereal rye (*Secale cereale* L.); SC, yellow blossom sweet clover [*Melilotus officinalis* (L.) Pall.]; TR, triticale (x *Triticosecale* Wittm. ex A. Camus.).

^bThe No Cover treatment in this experiment had significant weed growth, which was sampled and treated as winterhardy cover crop biomass.

soil C pool measured in the study soils. To use soil C concentration instead of soil N concentration, we add a term in Equation 3 that converts the C concentration to N concentration based on the N/C ratio of SOM, (N/C)_s. The soil sam-

ples from these experiments all had a C/N ratio [(C/N)_s] of approximately 10:1. This is similar to the composite microbial biomass C/N ratio that is often assumed in ecosystem C and N models. Treating both (C/N)_s and (C/N)_m as constant

values of 10 allows them to cancel each other out in Equations 2 and 3. The N/C ratio of SOM ($(N/C)_s$), if treated as a constant, can also be combined with the decomposition rate of SOM (k_s). Finally, we assume that the unfertilized corn yield (Y_s) will change proportionally to N mineralization from SOM and embed this yield response into a new empirical constant (α_s with units $\text{Mg grain g}^{-1} \text{ C } 100 \text{ g soil}$) that serves as a composite of both mineralization rate and yield response. These steps expand Equation 2 into Equation 3, which can then be simplified to Equation 4. Parameters in Equation 4 can be calibrated to predict an unfertilized corn yield based on a measurement of C_s (in units of $\text{g C } 100 \text{ g}^{-1} \text{ soil}$).

$$\Delta Y_s = k(N/C)_s C_s \left(1 - \frac{\varepsilon(C/N)_s}{(C/N)_m} \right) \quad (3)$$

$$\Delta Y_s = \alpha_s C_s (1 - \varepsilon) \quad (4)$$

The $\text{CO}_2\text{-C}$ flux during a 24-h incubation of a rewetted soil sample can also be formulated into a biogeochemical equation to predict N mineralization and yield of an unfertilized corn crop. In this case, microbial CO_2 respiration is a product of the C pool size (C_s), the decomposition rate (k_s), and the humification or C use efficiency (ε) as expressed in Equation 5 (Manzoni & Porporato, 2009).

$$\text{CO}_2\text{-C} = k_s C_s (1 - \varepsilon) \quad (5)$$

Rearranging Equation 5 (as in Equation 6) allows $\text{CO}_2\text{-C}/k_s$ to be substituted for $C_s(1 - \varepsilon)$ in Equation 4, yielding Equation 7. Equation 7 can be simplified by combining the constants α_s and k_s into a single empirical coefficient ($\alpha_{s\text{-CO}_2}$), for which the value can be determined through calibration. An important assumption of this approach is that the decomposition rate for the 24-h period measured in the laboratory incubation is proportional to the decomposition rate for SOM integrated across a corn growing season in the climate where the equation is being calibrated.

$$\frac{\text{CO}_2\text{-C}}{k_s} = C_s (1 - \varepsilon) \quad (6)$$

$$Y_s = \alpha_s \frac{\text{CO}_2\text{-C}}{k_s} = \alpha_{s\text{-CO}_2} \text{CO}_2\text{-C} \quad (7)$$

The humification efficiency, ε , is an important parameter regulating N mineralization in Equation 4. Theoretical and empirical evidence suggests that this parameter is sensitive to soil texture because clay minerals serve to stabilize soil C against microbial predation (Baldock & Skjemstad, 2000; Cotrufo, Wallenstein, Boot, Denef, & Paul, 2013; Schmidt et al., 2011). Indeed, many C and N cycling models use soil texture to regulate ε (Jenkinson, 1990; Kemanian & Stöckle,

2010; Parton et al., 1987; Verberne et al., 1990). Generally, ε increases with clay content and/or decreases with sand content, depending on the model. To incorporate this theoretical consideration into our calibration, we allowed ε to vary as a function of sand and clay content of the soil (Equation 8).

$$\varepsilon = \text{int} + b_{\text{clay}} \% \text{Clay} + b_{\text{sand}} \% \text{Sand} \quad (8)$$

2.3.2 | N mineralization from cover crop residues

Because cover crops were also included in these experiments, a previously calibrated equation to predict N availability from cover crop residues (White et al., 2016) was used to credit N availability from those residues in each experimental unit (Equation 9). Equation 9 predicts the change in unfertilized corn yield compared with a fallow treatment that will occur from N mineralization or immobilization of cover crop residues, where N_{wk} is the N content (kg ha^{-1}) of winterkilled cover crop residues measured in the fall; N_{whcc} is the N content (kg ha^{-1}) of winterhardy cover crop residues measured in the spring; $(C/N)_{\text{whcc}}$ is the C/N ratio of winterhardy cover crop residues measured in the spring; ε is the humification efficiency, which varies with soil texture (Equation 8); and α_{wh} is an empirically derived parameter representing the grain yield change per unit of N mineralization.

$$\Delta Y_{\text{cc}} = 0.0078 N_{\text{wk}} + \alpha_{\text{wh}} N_{\text{whcc}} \left(1 - \frac{\varepsilon(C/N)_{\text{whcc}}}{10} \right) \quad (9)$$

where $\alpha_{\text{wh}} = 0.026$ when cover crops are N mineralizing and $\alpha_{\text{wh}} = 0.085$ when N immobilizing.

In our calibration here, we retain the previously determined values of α_{wh} but refit ε to be dependent on soil texture. In our previous calibration of Equation 9 (White et al., 2016), the threshold for determining an N immobilizing cover crop was when $(C/N)_{\text{whcc}} > 10/\varepsilon$, where ε was a fixed value determined through the calibration process. Here, where ε is determined by soil texture, the threshold for an N-immobilizing cover crop is still $(C/N)_{\text{whcc}} > 10/\varepsilon$, but the numerical value of the $(C/N)_{\text{whcc}}$ above which the N-immobilizing condition is triggered will vary with soil texture.

2.3.3 | Total yield response to N mineralization from SOM and cover crops

The final step in the system of equations is to sum the yield responses promoted by N mineralized from SOM (ΔY_s) and cover crop residues (ΔY_{cc}) to determine the unfertilized corn yield. In this step, we allowed the total unfertilized corn yield (ΔY_t) to respond quadratically to the sum of yield responses caused by N mineralization from SOM and cover

crop residues (Equation 10). The quadratic response of corn yields to N additions is the most widely used yield response model (Morris et al., 2018), and including this feature in our model is a key step in addressing the limitations of the mass balance approach to N fertilizer recommendations where estimates of mineralized N linearly contribute to the overall N requirement of the crop (Rodriguez et al., 2019).

$$\Delta Y_t = b_1(\Delta Y_S + \Delta Y_{cc}) + b_2(\Delta Y_S + \Delta Y_{cc})^2 + b_0 \quad (10)$$

where $b_1 = 1$ to prevent auto-correlation with α_s , α_{s-CO_2} , and α_{wh} in Equations 4, 7, and 9, respectively.

2.4 | Model calibration

To calibrate these systems of equations and evaluate the accuracy with which unfertilized corn yield could be explained, we used the dataset of 73 observations from nine different cover crop experiments. We compared the explanatory and predictive accuracy of a system of equations using measurements of total soil C (Equations 4, 8–10) with a system of equations using the CO_2 respiration measurement (Equations 7–10). Unknown parameters in each system of equations were calibrated simultaneously with the NLMIXED procedure in SAS 9.4 (SAS Institute) using Newton–Raphson optimization techniques. For the Newton–Raphson optimization techniques to complete successfully, the line searching method was used for the total soil C model and the ridging method was used for the CO_2 respiration model. The NLMIXED procedure calculates maximum likelihood estimates of parameters, standard errors of parameter estimates, 95% CIs, and correlations of parameters. The parameters int , b_{clay} , and b_{sand} in Equation 8 were bounded to be positive, positive, and negative, respectively, and the quadratic coefficient b_2 in Equation 10 was bounded to be negative. Further, in the CO_2 respiration model, the calculated value of ϵ was bounded to a minimum value of 0.15 and a maximum value of 0.75. These bounds were implemented to prevent the optimization algorithm from wandering into local solutions that were suboptimal or not theoretically plausible.

To prevent model overfitting and improve parsimony, the predictive accuracy of the full model formulation and candidate reduced models were compared in a fivefold cross-validation. Observations from the full data set were randomly assigned to onefold of fivefold that were withheld from the model calibration and used as a test set to assess model accuracy at predicting blind observations during each round of the cross-validation. Criteria for removing parameters in candidate reduced models included if parameters were not significantly different than zero ($\alpha = .05$) or if parameters were correlated during the optimization process of the full model ($r > .5$). Parameters that are highly correlated may capture

redundant information about the same process and can also cause unstable parameter estimates. Accuracies of the reduced models were compared with the original model based on the RMSE of predictions on out-of-fold observations. and the model with the lowest RMSE was selected as the preferred model. Accuracy of the soil C concentration and CO_2 respiration models were compared with each other using the coefficient of determination and RMSE of the out-of-fold predictions during the cross-validation of the reduced models using the REG procedure in SAS 9.4 and by a calculation of Willmott's index of agreement (Willmott, 1981).

3 | RESULTS AND DISCUSSION

Experiments included in the calibration dataset exhibited a wide range of soil textures, soil C concentrations, CO_2 respiration rates, and unfertilized corn yields (Table 1). Across the experiments a wide range of cover crop types were also represented (Table 4), including pure grasses; pure legumes; and mixtures of grasses, legumes, and brassicas as well as plots with no cover crops planted. Soil nitrate-N concentration in the surface soil prior to cover crop termination and corn planting was relatively low ($<7 \text{ mg kg}^{-1}$), even in no-cover-crop plots (Table 4). Calibrated systems of equations (hereafter referred to as models) using either soil C concentration or 24 h CO_2 respiration as inputs were able to predict unfertilized corn yield with reasonable accuracy, although the soil C model was more accurate than the CO_2 respiration model (Figure 1; Table 5). Residuals of the predicted values were normally distributed in both models.

3.1 | Soil C concentration model

In the soil C concentration model, the parameter b_{clay} in Equation 8 predicting ϵ was not statistically significant ($P = .07$) and had a somewhat high correlation ($r = -.57$) with the intercept term in Equation 8. The intercept term (b_0) in Equation 10 also was not significant ($P = .11$) and was highly correlated to b_2 in Equation 10, α_s in Equation 4, and b_{sand} in Equation 8 ($r = -.97$, $-.93$, and $-.72$, respectively). The nonsignificant parameters were therefore removed to test a reduced model. The reduced model was slightly more accurate at predicting out-of-fold observations during the cross-validation (full model RMSE = 1.61 Mg ha^{-1} ; reduced model RMSE = 1.58 Mg ha^{-1}). In the reduced model, the only parameters that had correlations with each other greater than .5 were b_{sand} and the intercept term in Equation 8. These two terms in the equation of a straight line will naturally be correlated because the optimization algorithm adjusts the slope and intercept to find the best relationship between sand content and humification efficiency. Parameter estimates for

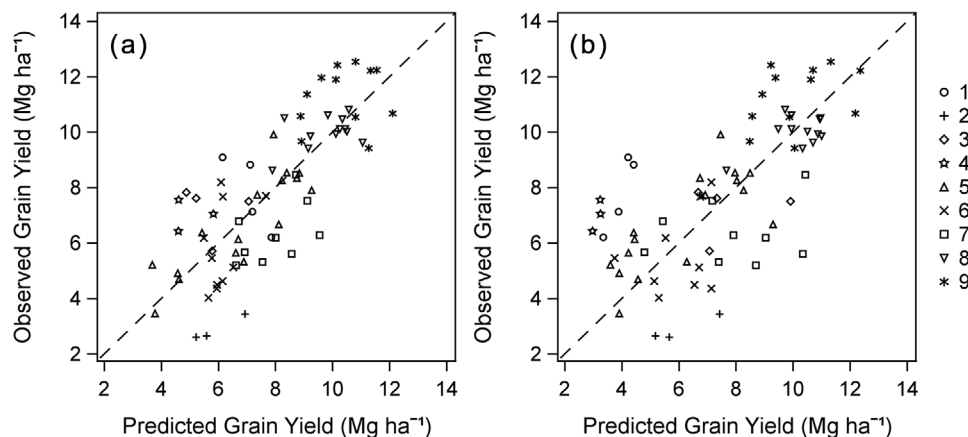


FIGURE 1 Relationships between predicted unfertilized corn yield and observed unfertilized corn yield for out-of-fold observations in the cross-validation of (a) the soil C model and (b) the CO₂ respiration model. The soil C model had an accuracy for predicting out-of-fold observations of RMSE = 1.58 Mg ha⁻¹, r^2 = .62, and Willmott's index of agreement = 0.87. The CO₂ respiration model predictive accuracy was RMSE = 1.87 Mg ha⁻¹, r^2 = .47, and Willmott's index of agreement = 0.81. Dashed lines are the 1:1 relationship, and symbols correspond to the experiment number of each observation

TABLE 5 Calibrated parameters for the systems of equations to predict unfertilized corn grain yields from inputs of either total soil C concentration or CO₂ respiration and sand content

Equation	Parameter	Estimate	95% CI	Parameter estimate in each cross-validation fold				
				1	2	3	4	5
Soil C (g 100 g ⁻¹ soil)								
Equation 8	int	0.774	0.59 to 0.96	0.717	0.764	0.898	0.741	0.747
	b_{clay}	Removed	–	–	–	–	–	–
	b_{sand}	–0.0157	–0.023 to –0.0082	–0.0133	–0.0152	–0.0210	–0.0141	–0.0149
Equation 4	α_{s}	9.85	7.6 to 12	9.92	9.93	9.67	9.86	9.68
Equation 10	b_2	–0.0217	–0.025 to –0.019	–0.0206	–0.0219	–0.0216	–0.0215	–0.0220
	b_0	Removed	–	–	–	–	–	–
CO ₂ respiration (mg C kg ⁻¹ dry soil 24 h ⁻¹)								
Equation 8	int	1.69	1.2 to 2.1	1.69	1.64	1.71	1.65	1.73
	b_{clay}	Removed	–	–	–	–	–	–
	b_{sand}	–0.0589	–0.079 to –0.039	–0.0592	–0.0566	–0.0597	–0.0572	–0.0598
Equation 7	$\alpha_{\text{s-CO}_2}$	0.0772	0.071 to 0.083	0.0778	0.0764	0.0767	0.0774	0.0773
Equation 10	b_2	Removed	–	–	–	–	–	–
	b_0	Removed	–	–	–	–	–	–

Note. Both models account for yield changes due to N mineralization or immobilization from cover crop residues using the previously calibrated Equation 9, except for allowing ϵ to vary with soil texture based on the calibrated Equation 8. Parameter estimates and 95% CI are for the reduced model formulations calibrated using all observations in the dataset. Parameter estimates during each fold of the fivefold cross-validation are also displayed to evaluate parameter stability.

the reduced model were highly stable across the five folds of the cross-validation (Table 5).

In the reduced formulation of the soil C concentration model, the soil sand percentage decreased the humification efficiency. Using the calibrated Equation 8, the calculated value for ϵ across the sites ranged from a minimum of 0.14

to a maximum of 0.56. Although this is consistent with ranges of microbial C use efficiency reported in the literature (Sinsabaugh et al., 2013), we caution against making direct comparisons between microbial C use efficiency values that represent a single generation of microbial predation and our use of the humification efficiency term here, which accounts

for multiple generations of microbial predation. An important implication of this variation in ϵ is that it changes the critical C/N ratio threshold for N immobilization from cover crop residues predicted by Equation 9. At $\epsilon = 0.14$, the critical threshold is 71:1, which is substantially greater than the critical threshold when $\epsilon = 0.56$, which is 19:1. In a previous model to predict N supply from cover crop residues, which we calibrated with experimental data conducted within a narrow range of soil types, the calibrated value for ϵ was 0.49 (White et al., 2016). The potential for the critical C/N ratio to change predictably based on soil sand content could help farmers fine tune cover crop management, such as termination date, to minimize N immobilization in a given field site.

The role of soil texture in the models is one component that could further be validated or refined. For instance, the current estimation of ϵ based on sand content would turn negative when sand content is greater than 49 g 100 g⁻¹ soil. The further elucidation of conceptual and quantitative differences between microbial C use efficiency and humification efficiency through additional controlled studies in the laboratory or field in a wide range of soil textures is also warranted. The role of C saturation, as mediated through soil texture, in controlling humification efficiency and N mineralization has been explored theoretically (White et al., 2014) and could also be tested in models such as these. Finally, the role of soil texture in affecting N use efficiency, such as increasing leaching losses in sandy soils or increasing denitrification in clayey soils, may need to be addressed in the parameters α_s and α_{wh} .

Total soil C concentration had a highly significant positive coefficient ($P < .001$) in Equation 4, capturing the role that SOM plays in supplying N to support the yield of an unfertilized corn crop. The effect of soil C concentration is regulated by the parameter ϵ , however, because C and N that are assimilated into microbial biomass or stabilized SOM during the decomposition process are not available to support crop growth. With soil texture regulating ϵ , each unit of soil C concentration will mineralize N and increase corn yield to a greater extent in a coarser-textured soil than in a finer-textured soil. Others have found similarly that net N mineralization, measured through corn N uptake, varies jointly with soil C and clay concentrations (Delin & Lindén, 2002). Tremblay, Bouroubi, Vigneault, and Bélec (2011) found that in field areas with high soil apparent electrical conductivity, a surrogate for clay concentration, corn growth mid-season was less and N fertilizer responsiveness was greater than in field areas with low apparent electrical conductivity. There is increasing recognition of the role that clay minerals play in stabilizing soil C (Baldock & Skjemstad, 2000; Cotrufo et al., 2013; Hassink, 1997; Schmidt et al., 2011), with further implications for N mineralization evidenced here. Despite this recognition and despite the inclusion of soil texture as a regulator of C use efficiency of C humification in many classic process-based models (Jenkinson, 1990; Parton et al., 1987; Verberne

et al., 1990), the two computer simulation models of N mineralization from cover crop residues reported in the literature used fixed values for C use efficiency (Melkonian et al., 2017; Woodruff et al., 2018).

In our study, we did not pretreat soil samples to remove carbonates prior to soil C analysis because fields had not received recent limestone applications and soil pH levels were all below 7.1. Previous research on using soil C to predict potential N mineralization has indicated that soils with a pH below 7.1 do not contain any carbonates (Jenkinson, 1968). However, consideration should be given to removing carbonates prior to soil C analysis in scenarios where they contribute substantially to soil C concentration because C in carbonate form does not contribute to N mineralization. Analyzing total soil N rather than total soil C could be an alternative methodology to avoid the confounding effect of carbonates and would also remove the assumption that SOM has a fixed N/C ratio across sites that we used when deriving our models. However, total soil N concentration can be quite low and may test the quantification limits of some combustion analyzers and/or suffer from low precision in the range of interest.

The quadratic term in Equation 10 was highly significant ($P < .001$), suggesting that increasing N mineralization from SOM and cover crop residues has diminishing returns to increasing corn yields. This is consistent with the commonly found quadratic yield response to inorganic N fertilizer additions (Cerrato & Blackmer, 1990; Morris et al., 2018) and with recent evidence that corn yields also respond nonlinearly to mineralized N (Franzluebbers, 2018). This feature of the system of equations also creates an interaction between the contributions of N mineralization from SOM and cover crop residues to the ultimate unfertilized corn yield. For instance, the effect of a given cover crop residue on the total unfertilized corn yield will diminish as soil C levels increase. Including a quadratic yield response to increasing N availability in the framework of our model is one important way in which our approach moves beyond N mass balance methods for crediting organic N sources, which have been heavily criticized (Morris et al., 2018; Rodriguez et al., 2019). A quadratic yield response to increasing N mineralization may also be one way in which the system of equations accounts for potential N losses from leaching and denitrification as the pool of mineral N increases.

3.2 | CO₂ respiration model

The CO₂ respiration model performed somewhat worse than the soil C model at predicting unfertilized corn yields (Figure 1). During calibration of the full model, the coefficient for the effect of clay content on ϵ in Equation 8 (b_{clay}) was pushed to its lower boundary condition of zero, indicating no effect. The quadratic term in Equation 10 (b_2) to

predict unfertilized corn yield based on the sum of N mineralized by cover crops and SOM also was not statistically significant for the CO₂ respiration model ($p = .36$) and was correlated with α_{s-CO_2} , the coefficient for CO₂ respiration in Equation 7 ($r = -.59$). The intercept term for the total yield response in Equation 10 (b_0), although highly significant, was also correlated with α_{s-CO_2} in Equation 7 ($r = -.90$). Based on these criteria, various combinations of the parameters b_{clay} in Equation 8 and b_2 and b_0 in Equation 10 were removed in the formulation of reduced models that were compared with the full model through the accuracy of fivefold cross-validations. The reduced model with all three of these parameters removed had the lowest RMSE (1.87 Mg ha⁻¹), which was lower than the RMSE of the full model (1.94 Mg ha⁻¹). Parameter estimates for the calibration of the reduced model based on all observations are presented in Table 5.

Our results for the accuracy of the CO₂ respiration model at predicting corn yield are not quite as accurate as the model developed by Franzluebbers (2018), where the r^2 varied from .5 to .6 depending on which soil sampling depth was used. Our respective studies used different laboratory assays of CO₂ respiration and different statistical models, which may partially explain the difference in the accuracy of the two studies. Franzluebbers used a 3-d incubation to measure CO₂ respiration, did not explicitly account for the effect of cover crop residues (which varied in their presence and in species across the sites), and used an exponential-plateau model to predict relative yield rather than a model derived from first-principles of biogeochemistry as we did.

3.3 | Comparison of soil C and CO₂ respiration model performance

It is remarkable that a relatively simple set of equations, based on biogeochemical theory and using routinely measured soil and plant analyses as input variables, could be calibrated to explain the majority of variation in unfertilized corn yields across numerous sites with different soil properties and in different growing seasons. Although both the soil C and CO₂ respiration models could be considered successful, the soil C model was more accurate in its predictions of unfertilized corn yield. One factor that could negatively affect the accuracy of the CO₂ respiration model is that a 24-h incubation period may not be as closely correlated to season-long C respiration as would be needed to rely on this assumption of proportionality when deriving a model as we have done here. The short duration of the 24-h respiration assay may be measuring a pool of highly labile C that could be exhausted over the course of a 4- to 5-mo growing season for corn. An incubation that measures intermediately labile C, such as the 3-d incubation used by Franzluebbers (2018), might increase the accuracy of the predictive model. Although 24-h CO₂ respiration

measurements are widely reported in the scientific literature (Curtin et al., 2017; Haney, Brinton, & Evans, 2008; Hurisso et al., 2016) and have been the most widely adopted method in the commercial soil testing industry due to expediency (Wade et al., 2018), other researchers have suggested using 72-h incubations for routine soil testing (Franzluebbers, 2016) and the commercially available Comprehensive Assessment of Soil Health suite of analyses uses a 96-h incubation time (Fine, van Es, & Schindelbeck, 2017). In Wade et al. (2018), a comparison of 24- and 72-h respiration periods found that the 72-h period was more sensitive to detecting treatment differences in long-term cropping system studies. Although there may be potential for improvement by using a longer incubation time, several studies have also demonstrated strong correlations between 24- and 72-h CO₂ respiration (Franzluebbers & Haney, 2018; Wade et al., 2018). Therefore, it is unclear whether longer incubation periods that are still within reason for use in routine soil testing would improve the accuracy of predictive models such as we have derived here.

Another factor that may reduce the accuracy of the CO₂ respiration model relative to the total soil C model is that mineralizable C and N from cover crop residues, which are being credited separately from mineralizable SOM pools in our system of equations, are possibly being measured as part of the 24-h CO₂ respiration. If this were the case, N availability from cover crop residues would be double counted in our system of equations. It is unlikely that a single year's cover crop residues are significant enough to influence the measurement of total soil C; however, it is quite possible that decomposing residues from spring terminated cover crops could influence the pool of mineralizable C measured in the 24-h CO₂ respiration assay because cover crops can have immediate impacts on microbial respiration rates (Finney, Buyer, & Kaye, 2017).

3.4 | Dependence of model calibration on regional soil and climate conditions

The formulation of the equations used in both the soil C and CO₂ respiration models is based on first principles of biogeochemistry, so the model structures should be translatable to different environments. However, because decomposition rates that control N mineralization and potential N losses that affect yield responses to mineralized N are affected by regional climatic and soil conditions, the calibrated values of parameters in the models from this study should not be extended to environments that are substantially different from the one in which this study was conducted. In the current study, monthly average air temperatures during the period in which cover crops were decomposing and corn was actively taking up N ranged from a low of 15.6 °C in May to a high of 25.3 °C in July to a low of 16.4 °C in September (Table 2). Precipitation in the humid mid-Atlantic region where this study

took place is generally evenly distributed throughout the year on average but can be quite variable from month to month depending on the location and year. In this study, the minimum cumulative monthly rainfall across sites during the corn growing season was 28 mm, and the maximum was 199 mm (Table 3). One shortcoming of the models presented here is that they are calibrated to average climatic conditions and so do not take into account real-time and site-specific variability in temperature and precipitation patterns as would a real-time dynamic simulation model. Real-time dynamic modeling might be able to better simulate N mineralization patterns and N losses as affected by interactions among climate and soil properties because it occurs over time at a given site year; however, such models require an extensive digital infrastructure for development and deployment.

Nitrogen available to support corn growth and yield can also accumulate in the soil profile in spring prior to corn planting. In some regions, pre-plant measures of soil profile nitrate concentration are used to adjust N fertilizer recommendations (Morris et al., 2018), but this is not commonly practiced in the humid mid-Atlantic region because winter precipitation levels usually leach residual soil nitrate below the corn rooting zone. Cover crops can also act as pre-emptive competitors to available inorganic N that may accumulate in the corn rooting zone in spring due to mineralization of SOM (Thorup-Kristensen, Magid, & Jensen, 2003). In our previous development of the cover crop N mineralization model (Equation 9), the pre-emptive competition effect of cover crops was accounted for by a calibration with parameters that decrease the N contribution of cover crops to support the yield of corn due to pre-emptive competition (White et al., 2016). In the study here, topsoil nitrate concentrations at corn planting were relatively low, ranging from undetectable in some grass monoculture cover crop treatments to $6.3 \text{ mg kg}^{-1} \text{ NO}_3\text{-N}$ in a fallow plot (Table 4). In climates or cropping systems where significant residual inorganic N accumulates prior to corn planting, this residual N may need to be accounted for in addition to N mineralized from cover crops and SOM during the growing season.

3.5 | Implications for N fertility management

It is well recognized that N mineralized from organic sources is an important contributor to the N nutrition of corn and that the inability to credit this indigenous N source is one of the factors leading to the low N use efficiency of inorganic N fertilizers (Cassman, Dobermann, & Walters, 2002). Despite a long-standing recognition of this problem, developing a method to predict soil N supply for use in adjusting an N fertilizer recommendation for corn has vexed the soil

fertility community since the advent of the Stanford equation (Morris et al., 2018; Stanford, 1973). The original formulation of the Stanford equation, which serves as the theoretical origin for most yield-based N fertilizer recommendation systems, proposed adding N fertilizer only to meet the additional N requirement of a crop that is not met by soil N. However, without an ability to predict soil N supply for a specific site, most yield-based N recommendation systems have simplified the Stanford equation to assume a constant level of soil N supply and calibrated the internal N requirement for a crop as a multiplier of the entire yield goal (Morris et al., 2018). Mass balance approaches to N fertilizer recommendations based on the Stanford equation have also been criticized for assuming linear relationships between the yield of a crop and the N uptake requirement because such an approach does not accurately portray or allow for the economic analysis of nonlinear yield responses to N additions (Rodriguez et al., 2019). Nitrogen mass balance approaches that account for N mineralization from cover crop residues or other organic N sources by linearly crediting mineralized N for fertilizer N may suffer from the overall weaknesses of such an accounting system.

We believe that the method of predicting N availability from cover crops and SOM presented here offers a novel step forward in N decision support tools. First, this approach answers the problem of predicting site-specific soil N supply capacity from organic N sources such as cover crops and SOM, which has stymied N fertilizer recommendation systems since their inception. Because our system of predictive equations is based on first principles of biogeochemical C and N cycling rather than simplified statistical models, the equations are robust in their ability to account for variations across site characteristics, such as soil texture, SOM content, and cover crop management practices. By directly predicting unfertilized corn yield with our system, rather than a quantity of mineralized N that substitutes for N fertilizer, and by allowing yield to respond quadratically to increasing N mineralization, we also overcome criticisms of the monotonic relationships between crop yields, N fertilizer requirements, and N credits that substitute for N fertilizer (Rodriguez et al., 2019). By calibrating our models to predict yield response rather than a pool size of mineralized N, our system is well positioned to integrate with existing and future N decision support tools focused on crop yield response rather than N mass balance accounting. The next step in developing this method is to determine how much fertilizer, manure, or other N amendments is needed to close the yield gap between an unfertilized crop, as predicted by the model, and the yield potential for a particular site and management context. We hope that an advance such as this can facilitate improvements in the N use efficiency, profitability, and environmental footprint of agro-economic production systems.

4 | CONCLUSIONS

We demonstrated that relatively simple biogeochemical models could be derived to predict the contributions of N mineralization from SOM and cover crop residues toward supporting the yield of corn. A model using measurements of total soil C and soil texture was more accurate than a model using 24-h CO₂ respiration of a rewetted soil. Transformative advances in N decision support have evaded agronomists for decades, leading to over-application of N in many cases (Robertson & Vitousek, 2009). The class of models developed here can support a new generation of N fertilizer recommendation systems that better account for the yield response of crops to N contributions from SOM and cover crop residues, with a goal of improving fertilizer N use efficiency, farming system profitability, and environmental quality.

ACKNOWLEDGMENTS

Financial support was provided by USDA-National Institute of Food and Agriculture Competitive Grant Agreements 2013-67019-21369, 2011-51300-30638, 2015-51300-24156, and 2019-68012-29904; USDA Northeast Sustainable Agriculture Research and Education grants SNE14-11, GNE11-017, and ONE17-306; and Hatch Appropriations under Projects #PEN04571 and #PEN04600, Accession #1003346.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

ORCID

Charles M. White  <https://orcid.org/0000-0002-3399-2777>

Denise M. Finney  <https://orcid.org/0000-0003-4322-0380>

REFERENCES

- Baldock, J., & Skjemstad, J. (2000). Role of the soil matrix and minerals in protecting natural organic materials against biological attack. *Organic Geochemistry*, 31(7–8), 697–710. [https://doi.org/10.1016/S0146-6380\(00\)00049-8](https://doi.org/10.1016/S0146-6380(00)00049-8)
- Bremner, J. M. (1965). Nitrogen availability indexes. In A. G. Norman (Ed.), *Methods of soil analysis. Part 2. Chemical and microbiological properties* (pp. 1324–1345). Madison, WI: ASA.
- Cassman, K. G., Dobermann, A., & Walters, D. T. (2002). Agroecosystems, nitrogen-use efficiency, and nitrogen management. *Ambio*, 31(2), 132–140. <https://doi.org/10.1579/0044-7447-31.2.132>
- Cerrato, M. E., & Blackmer, A. M. (1990). Comparison of models for describing corn yield response to nitrogen fertilizer. *Agronomy Journal*, 82(1), 138–143. <https://doi.org/10.2134/agronj1990.00021962008200010030x>
- Cotrufo, M. F., Wallenstein, M. D., Boot, C. M., Denef, K., & Paul, E. (2013). The Microbial Efficiency-Matrix Stabilization (MEMS) framework integrates plant litter decomposition with soil organic matter stabilization: Do labile plant inputs form stable soil organic matter? *Global Change Biology*, 19(4), 988–995. <https://doi.org/10.1111/gcb.12113>
- Curtin, D., Beare, M. H., Lehto, K., Tregurtha, C., Qiu, W., Tregurtha, R., & Peterson, M. (2017). Rapid assays to predict nitrogen mineralization capacity of agricultural soils. *Soil Science Society of America Journal*, 81(4), 979. <https://doi.org/10.2136/sssaj2016.08.0265>
- Delin, S., & Lindén, B. (2002). Relations between net nitrogen mineralization and soil characteristics within an arable field. *Acta Agriculturae Scandinavica, Section B — Soil & Plant Science*, 52(2), 78–85.
- Doane, T. A., & Horwath, W. R. (2003). Spectrophotometric determination of nitrate with a single reagent. *Analytical Letters*, 36(12), 2713–2722. <https://doi.org/10.1081/AL-120024647>
- Fine, A. K., van Es, H. M., & Schindelbeck, R. R. (2017). Statistics, scoring functions, and regional analysis of a comprehensive soil health database. *Soil Science Society of America Journal*, 81(3), 589–601. <https://doi.org/10.2136/sssaj2016.09.0286>
- Finney, D. M., Buyer, J. S., & Kaye, J. P. (2017). Living cover crops have immediate impacts on soil microbial community structure and function. *Journal of Soil and Water Conservation*, 72(4), 361–373. <https://doi.org/10.2489/jswc.72.4.361>
- Finney, D. M., White, C. M., & Kaye, J. P. (2016). Biomass production and carbon:nitrogen ratio influence ecosystem services from cover crop mixtures. *Agronomy Journal*, 108, 39–52. <https://doi.org/10.2134/agronj15.0182>
- Fox, R. H., Roth, G. W., Iversen, K. V., & Piekielek, W. P. (1989). Soil and tissue nitrate tests compared for predicting soil nitrogen availability to corn. *Agronomy Journal*, 81(6), 971–974. <https://doi.org/10.2134/agronj1989.00021962008100060025x>
- Franzluebbers, A. J. (2016). Should soil testing services measure soil biological activity? *Agricultural & Environmental Letters*, 1(1). <https://doi.org/10.2134/AEL2015.11.0009>
- Franzluebbers, A. J. (2018). Soil-test biological activity with the flush of CO₂: III. Corn yield responses to applied nitrogen. *Soil Science Society of America Journal*, 82(3), 708. <https://doi.org/10.2136/sssaj2018.01.0029>
- Franzluebbers, A. J., & Haney, R. L. (2018). Evaluation of soil processing conditions on mineralizable C and N across a textural gradient. *Soil Science Society of America Journal*, 82, 354–361. <https://doi.org/10.2136/sssaj2017.08.0275>
- Franzluebbers, A. J., Haney, R. L., Honeycutt, C. W., Schomberg, H. H., & Hons, F. M. (2000). Flush of carbon dioxide following rewetting of dried soil relates. *Soil Science Society of America Journal*, 64, 613–623. <https://doi.org/10.2136/sssaj2000.642613x>
- Gaskin, J. W., Cabrera, M. L., Kissel, D. E., & Hitchcock, R. (2020). Using the cover crop N calculator for adaptive nitrogen fertilizer management: A proof of concept. *Renewable Agriculture and Food Systems*, 35(5), 550–560.
- Haney, R. L., Brinton, W. H., & Evans, E. (2008). Estimating soil carbon, nitrogen, and phosphorus mineralization from short-term carbon dioxide respiration. *Communications in Soil Science and Plant Analysis*, 39(17–18), 2706–2720. <https://doi.org/10.1080/00103620802358862>
- Hassink, J. (1997). The capacity of soils to preserve organic C and N by their association with clay and silt particles. *Plant and Soil*, 191(1), 77–87. <https://doi.org/10.1023/A:1004213929699>
- Hurisso, T. T., Culman, S. W., Horwath, W. R., Wade, J., Cass, D., Beniston, J. W., ... Ugarte, C. M. (2016). Comparison of permanganate-oxidizable carbon and mineralizable carbon for assessment of organic matter stabilization and mineralization. *Soil Science Society of America Journal*, 80(5), 1352–1364. <https://doi.org/10.2136/sssaj2016.04.0106>

- Jenkinson, D. S. (1968). Chemical tests for potentially available nitrogen in soil. *Journal of the Science of Food and Agriculture*, 19, 160–168. <https://doi.org/10.1002/jsfa.2740190310>
- Jenkinson, D. S. (1990). The turnover of organic carbon and nitrogen in soil. *Philosophical Transactions of the Royal Society B: Biological Sciences*, 329(1255), 361–368.
- Kaye, J., Finney, D., White, C., Bradley, B., Schipanski, M., Alonso-Ayuso, M., ... Mejia, C. (2019). Managing nitrogen through cover crop species selection in the U.S. Mid-Atlantic. *PLOS ONE*, 14(4), 1–23. <https://doi.org/10.1371/journal.pone.0215448>
- Kemanian, A. R., & Stöckle, C. O. (2010). C-Farm: A simple model to evaluate the carbon balance of soil profiles. *European Journal of Agronomy*, 32(1), 22–29. <https://doi.org/10.1016/j.eja.2009.08.003>
- Khan, S. A., Mulvaney, R. L., & Hoeft, R. G. (2001). A simple soil test for detecting sites that are nonresponsive to nitrogen fertilization. *Soil Science Society of America Journal*, 65(6), 1751–1760. <https://doi.org/10.2136/sssaj2001.1751>
- Magdoff, F., Ross, D., & Amadon, J. (1984). A soil test for nitrogen availability to corn. *Soil Science Society of America Journal*, 46(6), 1301–1304. <https://doi.org/10.2136/sssaj1984.03615995004800060020x>
- Manzoni, S., & Porporato, A. (2009). Soil carbon and nitrogen mineralization: Theory and models across scales. *Soil Biology & Biochemistry*, 41(7), 1355–1379.
- Mazzilli, S. R., Kemanian, A. R., Ernst, O. R., Jackson, R. B., & Piñeiro, G. (2015). Greater humification of belowground than aboveground biomass carbon into particulate soil organic matter in no-till corn and soybean crops. *Soil Biology & Biochemistry*, 85, 22–30.
- Melkonian, J., Poffenbarger, H. J., Mirsky, S. B., Ryan, M. R., & Moebius-Clune, B. N. (2017). Estimating nitrogen mineralization from cover crop mixtures using the precision nitrogen management model. *Agronomy Journal*, 109(5), 1944–1959. <https://doi.org/10.2134/agronj2016.06.0330>
- Morris, T. F., Murrell, T. S., Beegle, D. B., Camberato, J. J., Ferguson, R. B., Grove, J., ... Yang, H. (2018). Strengths and limitations of nitrogen rate recommendations for corn and opportunities for improvement. *Agronomy Journal*, 110(1), 1–37. <https://doi.org/10.2134/agronj2017.02.0112>
- Parton, W. J., Schimel, D. S., Cole, C. V., & Ojima, D. S. (1987). Analysis of factors controlling soil organic matter levels in great plains grasslands. *Soil Science Society of America Journal*, 51, 1173–1179. <https://doi.org/10.2136/sssaj1987.03615995005100050015x>
- Robertson, G. P., & Vitousek, P. M. (2009). Nitrogen in agriculture: Balancing the cost of an essential resource. *Annual Review of Environment and Resources*, 34(1), 97–125. <https://doi.org/10.1146/annurev.enviro.032108.105046>
- Rodriguez, D. G. P., Bullock, D. S., & Boerngen, M. A. (2019). The origins, implications, and consequences of yield-based nitrogen fertilizer management. *Agronomy Journal*, 111(2), 725–735. <https://doi.org/10.2134/agronj2018.07.0479>
- Schmidt, M. W. I., Torn, M. S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I. A., ... Trumbore, S. E. (2011). Persistence of soil organic matter as an ecosystem property. *Nature*, 478(7367), 49–56. <https://doi.org/10.1038/nature10386>
- Schomberg, H. H., Wietholter, S., Griffin, T. S., Reeves, D. W., Cabrera, M. L., Fisher, D. S., ... Tyler, D. D. (2009). Assessing indices for predicting potential nitrogen mineralization in soils under different management systems. *Soil Science Society of America Journal*, 73(5), 1575. <https://doi.org/10.2136/sssaj2008.0303>
- Sinsabaugh, R. L., Manzoni, S., Moorhead, D. L., & Richter, A. (2013). Carbon use efficiency of microbial communities: Stoichiometry, methodology and modelling. *Ecology Letters*, 16(7), 930–939. <https://doi.org/10.1111/ele.12113>
- Sorensen, L. H. (1975). The influence of clay on the rate of decay of amino acid metabolites synthesized in soils during decomposition of cellulose. *Soil Biology & Biochemistry*, 7, 171–177.
- Sorensen, L. H. (1981). Carbon-nitrogen relationships during the humification of cellulose in soils containing different amounts of clay. *Soil Biology & Biochemistry*, 13, 313–321.
- Stanford, G. (1973). Rationale for optimum nitrogen fertilization in corn production. *Journal of Environmental Quality*, 2, 159–166. <https://doi.org/10.2134/jeq1973.00472425000200020001x>
- Thorup-Kristensen, K., Magid, J., & Jensen, L. S. (2003). Catch crops and green manures as biological tools in nitrogen management in temperate zones. *Advances in Agronomy*, 79, 227–302.
- Tremblay, N., Bouroubi, M. Y., Vigneault, P., & Bélec, C. (2011). Guidelines for in-season nitrogen application for maize (*Zea mays* L.) based on soil and terrain properties. *Field Crops Research*, 122(3), 273–283. <https://doi.org/10.1016/j.fcr.2011.04.008>
- Verberne, E. L. J., Hassink, J., De Willigen, P., Groot, J. J. R., & Van Veen, J. A. (1990). Modelling organic matter dynamics in different soils. *Netherlands Journal of Agricultural Science*, 38(3A), 221–238. <https://doi.org/10.18174/njas.v38i3A.16585>
- Wade, J., Culman, S. W., Hurisso, T. T., Miller, R. O., Baker, L., & Horwath, W. R. (2018). Sources of variability that compromise mineralizable carbon as a soil health indicator. *Soil Science Society of America Journal*, 82(1), 243. <https://doi.org/10.2136/sssaj2017.03.0105>
- White, C. M., DuPont, S. T., Hautau, M., Hartman, D., Finney, D. M., Bradley, B., ... Kaye, J. P. (2017). Managing the trade off between nitrogen supply and retention with cover crop mixtures. *Agriculture Ecosystems and Environment*, 237, 121–133. <https://doi.org/10.1016/j.agee.2016.12.016>
- White, C. M., Finney, D. M., Kemanian, A. R., & Kaye, J. P. (2016). A model–data fusion approach for predicting cover crop nitrogen supply to corn. *Agronomy Journal*, 108(6), 2527–2540. <https://doi.org/10.2134/agronj2016.05.0288>
- White, C. M., Kemanian, A. R., & Kaye, J. P. (2014). Implications of carbon saturation model structures for simulated nitrogen mineralization dynamics. *Biogeosciences*, 11(23), 6725–6738. <https://doi.org/10.5194/bg-11-6725-2014>
- Willmott, C. J. (1981). On the validation of models. *Physical Geography*, 2(2), 184–194. <https://doi.org/10.1080/02723646.1981.10642213>
- Woodruff, L. K., Kissel, D. E., Cabrera, M. L., Habteselassie, M. Y., Hitchcock, R., Gaskin, J., ... Rema, J. (2018). A web-based model of N mineralization from cover crop residue decomposition. *Soil Science Society of America Journal*, 82(4), 983–993. <https://doi.org/10.2136/sssaj2017.05.0144>

How to cite this article: White CM, Finney DM, Kemanian AR, Kaye JP. Modeling the contributions of nitrogen mineralization to yield of corn. *Agronomy Journal*. 2021;113:490–503. <https://doi.org/10.1002/agj2.20474>