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Nitrogen mineralization from organic materials and fertilizers: Predicting N release

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Abstract

Organic growers use a wide range of organic fertilizers and materials to supply nutrients and meet plant demand of N. These products range from commercially processed animal and plant byproducts to composts and poultry litters. To better synchronize N release with plant demand, we investigated the rate and pool of potentially mineralizable N from 22 commercial, organic fertilizers; 15 poultry litters; and 11 composts. Fertilizers and organic materials were mixed with soil and inorganic N was measured over 99 days under optimal conditions (50% estimated water holding capacity and 30°C). Net N mineralized from the organic fertilizer or material was determined and fit to first-order kinetics to determine the rate of mineralization (k) and the pool of mineralizable nitrogen (N0). Net N mineralized ranged from 25–93%, 10–55%, and 1–5% of the organic N applied for the fertilizers, poultry litters, and composts that mineralized, respectively. The pool of mineralizable N was accurately predicted from the initial total N of the materials, but no characteristics predicted the rate constant, k. Using a grouped approach based on product type and the percentage of N mineralized to determine k, we were able to predict net mineralized for fertilizers $(R^2 = 0.84)$ and poultry litters $(R^2 = 0.62)$.

1 | INTRODUCTION

Soil nutrient management is one of the most complex issues facing organic producers (Berry et al., 2002; Gale et al., 2006; Hartz & Johnstone, 2006; Pang & Letey, 2000). To meet plant demand for nutrients, organic farmers rely on soil organic matter, cover crops, composts, manures, and commercial fertilizers to supply plant nutrients (Gaskell & Smith, 2007). Organic fertilizers and materials used in organic farming are limited by the USDA National Organic Program Standards to sources bound primarily in organic forms, which must undergo mineralization before becoming plant available inorganic forms (inorganic exceptions allowed for N fertilizer

Abbreviations: Nmin, nitrogen mineralization; PAN, plant available nitrogen.

use: sodium nitrate, National Organic Program, 2019). Therefore, understanding the available pool and the rate of release of nutrients, especially nitrogen (N) from organic fertilizers and materials is critical to efficient production practices with reduced environmental impact (Gordillo & Cabrera, 1997; Hartz & Johnstone, 2006; Rosen & Allan, 2007).

Nitrogen is often the most limiting nutrient to yield in organic production due to a lack of synchronicity between mineralization and plant demand and its potential for loss through a variety of mechanisms (immobilization, leaching, gaseous losses) (Berry et al., 2002; Pang & Letey, 2000; Rosen & Allan, 2007; Timisina, 2018). The rate and amount of N mineralization from organic fertilizers and materials is a function of environmental conditions and material composition (Agehara & Warncke, 2005; Bi & Evans, 2010; Stadler et al., 2006). Field conditions (soil temperature

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and water content) drive microbial/enzymatic reactions that control mineralization and determine the amount of N released to plants, but the potential amount of N available for mineralization and its rate vary from product to product. Initial characteristics such as initial inorganic N, total N, the composition and complexity of N containing compounds, the carbon to N ratio, and the preparation of the material drive potential N availability and the optimal rate of mineralization (Douglas & Magdoff, 1991; Franklin et al., 2015; Gaskell & Smith, 2007; Gordillo & Cabrera, 1997; Hartz & Johnstone, 2006).

A wide range of organic products are available to supply plant available N, from commercially produced fertilizers, poultry litters, and composts (shipped in or produced onfarm). The nutrient composition of these materials are as variable as the products themselves. Commercial fertilizers, commonly made from animal and seed byproducts, can have initial total N concentrations from 2% (steamed bone meal) to 14-15% N (feather and porcine blood meal). These products can be processed (hydrolyzed, ground, mixed, and/or pelletized) or "as is" products. Fertilizer processing and preparation affects the total N concentrations, initial inorganic N, and the rate of N release (Gale et al., 2006; Hadas & Kautsky, 1994). Initial total N in poultry litter has been shown to range from 2– 6%, with much of the organic N in the form of easily degradable uric acid and urea (Nicholson et al., 1996; Stephenson et al., 1990). Nitrogen present in litter, and therefore potentially available N, varies widely based on layer versus broilers, feed, housing and storage conditions (Gordillo & Cabrera, 1997; Mowrer et al., 2014; Nahm, 2005; Stephenson et al., 1990). Similarly, total N in compost can be highly variable (less than 1 to 9%) depending on materials used, composting conditions, and compost maturity (Douglas & Magdoff, 1991; Franklin et al., 2015; Gale et al., 2006). Composts typically contain highly stabilized N compounds leading to low mineralization rates or immobilization (Hartz & Johnstone, 2006).

Some studies have investigated the pools and rate of N mineralization from these organic fertilizers and materials. Gordillo and Cabrera (1997) investigated the rate of N mineralization from 15 different broiler litter samples. Net N mineralized from these broiler litters fit well to two-pool, first-order kinetics, with the fast pool of mineralization (3.6– 30.3 g N kg⁻¹ litter) correlated to uric acid concentration and no significant differences in the slow pool among poultry litters. Net N mineralization ranged from 27-91% of the total N applied and correlated to the chemical indices uric acid, total N and the C/N ratio ($R^2 = 0.81$ to 0.95). Franklin et al. (2015) determined that from 14 different composts and soil conditioners the initial organic N and C/N ratio of the materials explained 83% of the variability observed for immobilization and mineralization. For composts that did mineralize, the group determined that between 4-17% of the total N applied became plant available.

Core Ideas

- Organic farmers use a wide variety of organic materials to supply N
- Fertilizers, litters, and composts range in their rate and amount of N mineralized
- Predicting N mineralization is crucial to synchronize release with demand

Nitrogen mineralization and the kinetics of N mineralization have been investigated for a few commercially available, organic fertilizers, like blood meal, alfalfa meal, feather meal, fish products (Agehara & Warncke, 2005; Gale et al., 2006; Hadas & Kautsky, 1994; Hartz & Johnstone, 2006). However, few of these studies attempted to predict the kinetics parameters of mineralization from chemical indices of N mineralization. These studies have shown that mineralization even from commercial products is highly variable, from 30-70% of the total N applied, and some cite different rates and pools for the same listed material. Due to the inherent differences in these materials based on source and processing, N mineralization rates may need to be characterized on an individual basis. Additionally, as organic production becomes more and more predominant, new materials are constantly being released that must be measured. Gaskell and Smith (2007) cite the need for addressing variability in these products to add precision for the organic producers reliant on them. Although long term incubations give valuable data on the pool of N mineralization and the rate of mineralization, these can be time-consuming and labor-intensive processes. Determining kinetic parameters of N mineralization with easily measurable chemical indices will allow for better prediction of plant available N from these materials.

Understanding the rate of N mineralization from organic fertilizers and materials will lead to better plant synchronization with N uptake and reduced losses, but to be practical to producers we need to be able to determine or predict these parameters quickly. Therefore, the objective of this study was to (i) determine the rate and pool of mineralizable N from a wide range of fertilizers, poultry litters, and composts commonly used by organic farmers (ii) determine if rate constants of mineralization and mineralization pools can be predicted by the initial characteristics of the material.

2 | MATERIALS AND METHODS

2.1 | Soil and material collection and initial characteristics

Soil was collected from the upper 20 cm of an area mapped as a Cecil sandy loam (fine, Kaolinitic, thermic Typic

Kanhapudult; NRCS, 2019) at the University of Georgia Durham Horticulture Certified Organic Farm (Watkinsville, GA). The soil was air dried (23°C) and passed through a 2-mm sieve prior to use and analysis. The maximum water holding capacity was estimated through saturation and draining over a sand bath for 48 h (Priha & Smolander, 1999; Wynagaard et al., 2018) and averaged 0.31 \pm 0.009 g H₂O g⁻¹ soil for the four replications. Particle-size distribution was determined using the hydrometer method (Gee & Or, 2002) and soil pH measured at 1:1 ratio in 0.01 M CaCl₂ (Miller & Kissel, 2010). The soil had an average pH of 5.2, 869 g sand kg^{-1} , 59 g clay kg^{-1} , and 74 g silt kg^{-1} . Total C and N were determined by dry combustion (Kirsten, 1979). The initial inorganic N of the soil was measured using 1 M KCl extraction (5 g soil to 40 ml KCl; Mulvaney, 1996), followed by colorimetric determination (Crooke & Simpson, 1971; Keeney & Nelson, 1982), and measured 0.5 mg NH_4 –N kg⁻¹ soil and 62 mg NO₃–N kg⁻¹ soil.

Organic materials were collected from local and national sources. Commercially available fertilizers were sourced through a variety of online retailers. Poultry litters were randomly collected from samples received from the University of Georgia Agricultural and Environmental Services Laboratories (AESL) and due to the collection/submission process, the origin, history, or age of the litter were unknown. Composts were collected from local farms, from samples collected at the University of Georgia AESL (same procedure as poultry litters), and purchased through big box retailers. Materials underwent routine analysis at the University of Georgia AESL for total Ca, K, Mg, Mn, Fe, Al, B, Cu, Zn, Na, S, and P (USEPA, 1996, 2007a, 2007b). Total N and C were determined by dry combustion (Kirsten, 1979). Gravimetric water content was determined by drying at 65°C for 48 h. Initial inorganic N was determined on fresh materials in 1 M KCl (ratios used for each material 1:200 for fertilizer (exception 0.5 g NaNO₃ to 200 ml), 2:200 for poultry litter, and 10:100 for compost). Samples were shaken for 30 min, centrifuged for 20 min, and then passed through a 0.45-µm filter over vacuum, followed by colorimetric determination for NO₃-N and NH₄–N (Crooke & Simpson, 1971; Keeney & Nelson, 1982). Initial characteristics of the materials are presented in Table 1.

2.2 | Laboratory incubation study

To determine the rate of mineralization/N release from 47 organic materials (and one inorganic material), a long-term (99 d) incubation was performed. To avoid the potential for rewetting of the soil to cause a flush of mineralization (Cabrera, 1993), soil was rewetted to 50% estimated water holding capacity, 0.15 g H₂O g⁻¹ dry soil, and allowed to pre-incubate under aerobic conditions for 4 weeks. The water content at the start of the experiment was determined to be 0.14 g H₂O g⁻¹ dry soil (105°C for 48 h). Organic mate-

rials were added at variable rates to provide an estimated 150 mg kg⁻¹ soil of plant available N based on the assumption that 50% of total N was available from commercial fertilizers, 10% was available from compost, and 45% was available from poultry litter (Gale et al., 2006). The material was added to 300 g dry equivalent soil in 0.9-L mason jars and mixed thoroughly. Mason jars were placed in an incubator at 30°C (Cassity-Duffey et al., 2017), jars were aerated and water content maintained gravimetrically every few days. To determine the rate of release of inorganic N over time, 5-g subsamples were taken at 1, 3, 7, 14, 35, 56, 78, and 99 d and were extracted with 40 ml 1 M KCl, shaken for 30 min and passed through a Whatman #42 filter. Prior to sub-sampling, soils were thoroughly mixed to avoid sampling heavily concentrated areas of fertilizers. Inorganic N was determined colorimetrically (Crooke & Simpson, 1971; Keeney & Nelson, 1982). Gravimetric water content was determined at d 99 (105°C for 48 h) and the remaining soil was air-dried in paper bags and stored.

2.3 | Mineralization kinetics and statistics

Inorganic N on a dry weight basis for each sampling period was calculated using the water content determined at 99 d (a few of the additions, especially the composts, altered the water content of the soil from 0.10 to 0.21 g $\rm H_2O~g^{-1}$; but the average of all treatments was 0.14 g $\rm H_2O~g^{-1}$). Net N mineralized from the materials at each sampling time (dx) was calculated by subtracting the net N mineralized from the control and the initial inorganic N applied from the treated sample as follows:

Net N mineralized = Inorganic
$$N_{(dx)}$$
 - Inorganic N control_(dx) - Initial inorganic N in the material (1)

Net N mineralized was expressed as grams of N per kilogram of dry material and as a percentage of total organic N applied, where organic N was calculated as the difference between the total N and inorganic N of the material.

To determine N mineralization kinetics, net N mineralized (g N kg^{-1} dry material) was fit to one-pool first-order kinetics using non-linear regression:

Net N mineralized

$$(g \text{ N kg}^{-1}\text{dry material}) = \text{N0} \times (1 - e^{-kt})$$
 (2)

where N0 is the pool of mineralizable N (g N kg⁻¹ dry material), k is the rate constant of mineralization (d⁻¹), and t is time in days. To determine differences in mineralization parameters among materials, residual sum of squares of analysis (Miliken & Debruin, 1978) was used to assess if the fitted lines of individual materials were significantly different from a common model for all materials ("full model"). For

TABLE 1 Initial characteristics measured in organic fertilizers and materials used in the study with net N mineralization values (99 d) and parameters fit to first-order mineralization kinetics

							Plant available			
	Total C	Total N	NH ₄ -N	NO ₃ -N	Net Nmin	Net Nmin	N^a	N0	k	\mathbb{R}^2
	g kg ⁻¹ mat (% organic		mg kg ⁻¹ m	naterial	g kg ⁻¹ material	% organic N applied	% total N applied	g kg ⁻¹ material	d^{-1}	
Poultry litters										
PL1	254	31 (78)	6967	10	5.0 ± 0.5	20.3	38.0	Nofit ^c	-	-
PL2	366	37 (82)	5265	1182	4.4 ± 1.1	14.7	29.7	Nofit	-	-
PL3	346	44 (83)	5596	1757	12.1 ± 1.4	33.2	44.4	14.1	0.03	0.83
PL4	376	36 (83)	5872	161	3.0 ± 1.3	9.7	24.7	Nofit	-	-
PL5	396	47 (84)	7579	11	7.7 ± 0.2	19.5	32.5	8.1	0.03	0.74
PL6	318	39 (85)	5661	834	7.4 ± 0.5	22.6	35.4	Nofit	-	-
PL7	347	37 (84)	4667	929	17.7 ± 0.2	55.2	56.6	44.4	0.005	0.94
PL8	420	52 (84)	8127	3	8.9 ± 2.1	20.1	32.5	11.3	0.12	0.30
PL9	338	42 (86)	5447	567	14.2 ± 3.8	39.2	47.9	24.1	0.01	0.68
PL10	282	43 (89)	4123	553	14.2 ± 2.6	37.2	38.9	11.9	0.19	0.58
PL11	344	40 (83)	6080	656	13.0 ± 5.1	39.2	49.5	14.3	0.03	0.70
PL12	387	46 (84)	5671	1512	9.8 ± 0.3	25.3	37.1	11.0	0.03	0.83
PL13	405	41 (71)	11578	29	11.5 ± 0.3	39.2	56.6	13.8	0.02	0.7
PL14	428	55(87)	6754	3	12.4 ± 2.5	25.8	34.9	No fit	-	-
PL15	374	39 (84)	5075	1007	5.9 ± 2.1	17.8	30.6	No fit	-	-
Composts										
C1	337	31 (98)	54	609	0.75 ± 0.5	2.4	4.5	No fit	-	-
C2	524	41 (89)	4651	9	1.8 ± 0.5	4.8	15.7	No fit	-	-
C3	235	8 (99)	38	0	Immob.d	Immob	-	-	-	-
C4	171	16 (96)	22	622	0.2 ± 0.2	1.3	5.3	0.40	0.10	0.23
C5	298	3 (99)	16	0	Immob.	Immob	-	-	-	-
C6	266	16 (100)	5	30	Immob.	Immob	-	-	-	-
C7	281	25 (97)	8	645	0.82 ± 0.3	3.2	5.7	0.96	0.04	0.28
C8	507	11 (93)	22	747	Immob.	Immob	-	-	-	-
C9	229	10 (99)	6	104	Immob.	Immob	-	-	-	-
C10	200	13(98)	7	230	0.38 ± 0.2	2.7	4.4	0.22	2.94	0.15
C11	348	19 (95)	902	99	0.87 ± 0.02	4.6	9.4	0.53	0.46	0.13
Fertilizers										
NaNO ₃	3	153 (na)	92	147119	na	na	95.9	na	-	-
Blood meal	548	144 (94)	8964	27	124.6 ± 9.6	92.3	92.7	109.7	0.10	0.89
Feather meal	552	154 (99)	1080	5	118.9 ± 7.5	77.8	88.9	104.1	0.15	0.93
Fish meal	449	113 (92)	9179	12	84.5 ± 3.5	28.8	83.5	75.3	0.15	0.82
Crab shell	262	48 (91)	3871	24	27.5 ± 3.6	62.4	65.4	22.5	0.60	0.79
Alfalfa meal	477	30 (85)	3688	646	Immob.	-	-	-	-	-
Fish mixe	375	82 (90)	7381	72	61.8 ± 6.6	82.9	84.5	45.4	0.17	0.74
Mustard seed	541	63 (98)	1367	13	14.5 ± 7.8		25.1	Var.g	-	-
Veggie mix ^e	396	76 (93)	942	29	61.1 ± 11.7	82.2	80.1	65.8	0.03	0.92
AllPur. mixe	261	54 (93)	3998	57	39.8 ± 0.8	79.1	81.4	33.5	0.13	0.80
Fish bone	269	70 (88)	8089	9	50.8 ± 2.1	81.7	84.4	41.0	0.37	0.8
Bone meal	194	54 (100)	29	5	13.4 ± 1.4	24.7	24.8	9.6	0.24	0.49
Cotton seed	481	87 (83)	14788	44	43.2 ± 1.8	59.8	43.2	33.7	0.09	0.77

(Continues)

TABLE 1 (Continued)

							Plant available			
	Total C	Total N	NH ₄ -N	NO ₃ -N	Net Nmin	Net Nmin	N^a	N0	k	\mathbb{R}^2
Mix 1 ^e	384	78 (99)	423	63	41.3 ± 3.7	53.3	53.5	34.8	0.09	0.75
Mix 2 ^e	311	72 (99)	455	2	46.2 ± 3.0	64.2	64.4	41.4	0.05	0.79
Mix 3 ^e	417	106 (100)	455	56	64.9 ± 1.5	61.2	61.3	53.2	0.10	0.89
Pellet 1 ^e	368	39 (86)	5267	359	11.8 ± 0.9	34.5	44.8	16.2	0.02	0.38
Pellet 2 ^e	485	91 (97)	2444	180	37.9 ± 5.2	42.9	44.6	108.4	0.004	0.79
Pellet 3 ^f	245	39 (83)	5884	718	9.9 ± 2.4	30.3	42.1	Var.	-	-
Pellet 4 ^f	292	48 (81)	9043	266	9.9 ± 7.6	25.5	40.0	Var.	-	-
Pellet 5 ^f	358	53 (90)	5382	20	13.7 ± 1.6	28.8	36.1	12.3	0.05	0.69
Pellet 6 ^f	332	54 (91)	5401	34	21 ± 1.9	43.0	48.4	15.2	0.29	0.67

^aPlant Available N (PAN) is the sum of net N mineralized and the initial inorganic N.

the residual sums of squares analysis, materials were grouped by product type (fertilizer, poultry litters, or composts).

To include the initial inorganic N supplied from the application of the materials and the N that mineralized during the incubation, the plant available N as a percentage of the total N applied (PAN, %) was also calculated as follows:

PAN,
$$\% = (\text{Net Nmin}_{99d} + \text{Initial inorganic N})/\text{Total}$$

N applied
$$\times$$
 100 (3)

First-order kinetics of mineralization were fit using PROC NLIN (SAS, 2016) with the pseudo R^2 calculated as $\{1 - (\text{residual sum of squares/corrected sums of squares)}\}$. Relationships between N mineralization parameters (net Nmin, N0, and k) and initial characteristics of the materials were determined using PROC REG (SAS, 2016) for individual parameters. The STEPWISE SELECTION was used to identify material characteristics that may lead to prediction of the parameters from multiple regression equations (default p < .15 for initial selection). To determine the goodness of fit for predicted parameters, modeled versus measured values were regressed using PROC REG (SAS, 2016).

3 | RESULTS AND DISCUSSION

3.1 | Nitrogen mineralization: Incubation experiment

Nitrogen mineralization in the control soil followed zerokinetics similarly to Cabrera (1993) where net Nmin (mg kg⁻¹ soil) = 2.27 + 0.605d with a R² of 0.91 and d is the number of days. The soil inorganic N increased from 63 mg inorganic N kg⁻¹ soil to 128 mg inorganic N kg⁻¹ soil over the 99-d study, for a net mineralization of 65 mg of inorganic N per kilogram of soil. This value is greater than those typically reported for soils in the region (Cabrera, 1993). The soil was collected from an organically managed farm (11+ years) with intensive cover crop rotations and organic amendment additions, which led to a buildup of soil organic matter as reflected in the total C (2.3%) and total N (0.19%) of the soil. Organic management has been shown to increase the N potential of soils through increased organic matter accumulation and enhanced microbial activity (Briar et al., 2007; Marriot & Wander, 2006).

Nitrogen release of the NaNO₃ fertilizer served as a reference throughout the 99-d study. Over the eight sampling periods, recovery of NaNO₃ averaged 96% of applied N. Greater variability was observed for the NaNO₃ treatment among replicates during Days 1, 3, and 7 (with coefficients of variation of 0.29, 0.26, and 0.17 respectively) likely due to a lack of uniformity of the mixture. This trend was observed with some of the organic materials as well. With the materials applied "as is" (unground), it likely took time for the materials to become evenly dispersed throughout the soil, even with mixing at sub-sampling and at time of water additions. This was especially evident with the very large pelleted materials, mustard meal and pellet poultry 3 and 4, where high variability among reps in the first sampling periods inhibited the fit of first-order kinetics (Table 1).

A wide range of N mineralization/immobilization was observed from the organic materials as shown in Table 1.

^bPercent organic N of total N is presented in parenthesis next to Total N values.

^cNo fit, the net N mineralization of the materials could not be fit to the first order kinetic model.

^dImmob., the material showed immobilization.

^eMixes containing animal, bone, and blood meal.

fMixes containing pelleted poultry litter and/or other animal and bone meals.

g Variable indicates that the data collected from the material had too much variation to be fit to the first order kinetic model.

Net N mineralization as a percentage of the total organic N applied ranged from 25–92% for the commercially available fertilizers. Of the 22 fertilizers, only the application of alfalfa meal led to the immobilization or possible losses through denitrification of N, which was observed beginning at 3 d and at each subsequent sampling point up to 99 d. This is in contrast to results from Agehara and Warncke (2005) who determined net N mineralized over 12 weeks to be 52% of the total N applied for ground alfalfa pellets. The alfalfa meal in their study had a C/N ratio of 11.1, less than the C/N ratio of 16.1 in our study. The alfalfa meal had the highest C/N ratio of all the fertilizers used and was above the threshold for net N mineralization observed in this study (C/N ratio less than 11). Additionally, the alfalfa meal used in our study was characterized by high NO₃-N concentrations (646 mg⁻¹ kg material), indicating that the material may have undergone mineralization prior to packaging. For all materials measured, NH₄-N dominated the inorganic nitrogen present during the first 7 days after application, likely due to the high levels of initial NH₄-N in the materials. By day 14, however, NO₃-N was the dominate species and NH₄-N approached zero.

Net N mineralized was greater than 70% of the organic N applied for blood meal, feather meal, fish meal, fish mix, veggie mix, all-purpose mix, and the fish bone meal. All the mixes contained both feather and blood meal, but the proportions are proprietary. These materials showed rapid net mineralization, with more than 30% of the organic N applied made available in the first 3 days and 45% in the first 14 d, with the exception of the veggie mix (examples in Figure 1a). Similar values in mineralization and the rate of release for feather meal, blood meal, and fish meal have been previously described (Agehara & Warncke, 2005; Gale et al., 2006; Hadas & Kautsky, 1994; Hartz & Johnstone, 2006). The total PAN (%) was highest in the blood meal, likely due to the relatively high initial inorganic N content. Hartz and Johnstone (2006) attributed the fast mineralization of fish, feather, and blood meal in the first two weeks to enzymatic hydrolysis of easily degraded N-compounds and the later, slower degradation of more complex, organic forms by the microbial community. In contrast, for feather meal, Hadas and Kautsky (1994) saw an initial increase in bacteria 1 d after application and a second pulse of bacterial growth observed at 14 d. The group cited slower release later in their study to be caused by microbial incorporation and subsequent N release due to the secondary decomposition of microbially related N. Material size of these products (finely ground, processed/hydrolyzed) combined with high initial total N concentrations favored low C/N ratios and accessibility to organic N for enzymes and microorganisms.

The remaining 11 fertilizers showed intermediate or low net mineralization comparatively (Table 1). These materials were highly variable in their composition. Bone meal, which is typically applied to meet phosphorous needs, showed 25% of the organic N applied mineralized. The mixes 1, 2, and 3 showed intermediate release in the first 14 d, likely due to the rapid mineralization of blood and feather meal included in the mixes (example Figure 1a). Of interesting note is the net N mineralized from the crab shell meal, which amounted to 62% of the organic N applied. It rapidly released N in the first week, which was unexpected due to the high chitin content of the shells that would be expected to resist microbial degradation. Six of the fertilizers were pelleted poultry manure (some fortified with other amendments to increase the N content) and net N mineralized from these materials ranged from 9.9 to 37.9 g N kg⁻¹ material. Hadas et al. (1983) determined rapid mineralization was completed earlier in ground manures compared to pelletized manures, citing the smaller surface area of the manure pellets and slower diffusion of the soluble organic compounds from the pellets for the delay in mineralization. In their study, Hadas et al. (1983) determined PAN for pelleted poultry litter was 42–50% of applied N, with rapid release observed in the first 7 d (38-42% PAN). While Nmin values were similar after 99 d, N release was slower in our study with an average of 21% of PAN available in the first 7 d (examples in Figure 1a). Many of the commercial fertilizers used in this study have not been previously studied for N mineralization or fertilizer N equivalents.

Net N mineralized from poultry litters ranged from 3-17.7 g kg⁻¹ material (10–55% of organic N applied) over the 99 d (Table 1). The poultry litters used in this experiment had an average net mineralization of 9.8 g kg⁻¹ material and total PAN (mineralized N plus initial N) averaged 39.2% of total N applied. For 5 of 15 litter materials, immobilization of N was observed during the first few weeks after application, but over the 99-d period these rebounded with net N mineralized. Differences were observed in the rate of mineralization, with some litters, like PL10, rapidly releasing N in the first 14 d and others, like PL7, having slower, later, and more linear release (Figure 1b). This is contrasting to previous reported values (Gordillo & Cabrera, 1997; Qafoku et al., 2001; Ruiz Diaz et al., 2008), where net N mineralized from poultry litter was measured to be near or greater than 50% of the organic N applied and mineralization occurred rapidly in the few first weeks. Similar to results determined in this study, Mowrer et al. (2014) determined some immobilization and comparatively lower mineralization from 50 different litters. Those authors determined net N mineralization from -2.1 to 12.7 g N kg⁻¹ material with an average of 7.4 g N kg⁻¹ material over 100 d. Mowrer et al. (2014) cited that differences in fresh, composted, or stacked litter for the lower mineralization observed in their study, with raw litter likely to have a larger pool of mineralizable N and more rapid mineralization due to the higher amounts of easily degradable uric acid and urea. Due to the anonymous collection process of our samples, no information on litter production, age, or storage is available

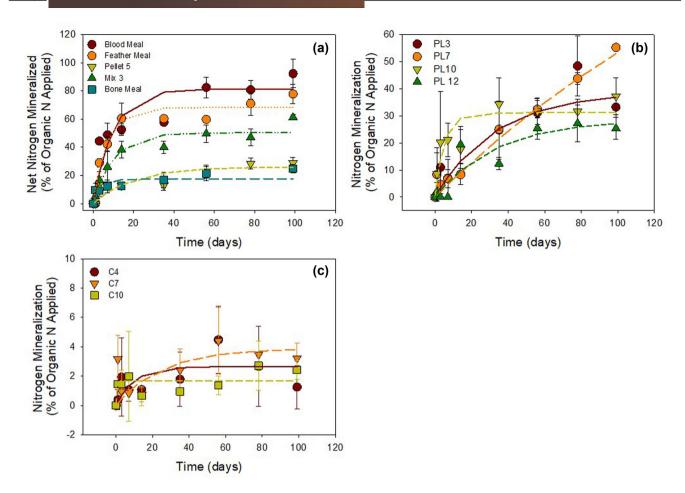


FIGURE 1 Net N mineralization determined through 99-d incubation as a percent of the total N applied for selected fertilizers (a), poultry litters (b), and composts (c) measured in this study

but from the relatively low values of mineralization and already high value of NH₄–N (Table 1), it is likely than many of these were not collected fresh from the house and underwent some period of storage. The wide variation in mineralization reported here and in the literature highlights the need for the testing of individual litters prior to application for appropriate rate recommendations. Further, variation in these data suggests that blanket estimates of available N can easily lead to over or under application of N from poultry litter.

Of the 11 composts studied, five showed immobilization of N (Table 1; Figure 1c). These composts were characterized by high C/N ratios, from 17 to 104, indicating immature composts and following trends typically cited in the literature (Flavel & Murphy, 2006; Franklin et al., 2015). A compost C/N ratio of 12 has been suggested to indicate maturity by Bernal et al. (1998) and immobilization/mineralization trends in composts used in this study followed that trend with the exception of C11, which showed a small amount net mineralization with a C/N ratio of 18. This compost however was characterized by relatively high NH₄-N and was comprised of composted sewage sludge. It may have been that the quality of the C and N in this material, as

opposed to the ratio, that played a role in mineralization (Flaval & Murphy, 2006). Overall, from the six composts that mineralized, net N mineralized ranged from 0.2 to 1.78 g N kg⁻¹ material, averaging 0.8 g N kg⁻¹ material (3% of the applied organic N). Results of this study reiterated the low N availability of composts and the potential for immobilization from these materials (Franklin et al., 2015; Gale et al., 2006).

3.2 | Nitrogen mineralization kinetics and modeling

Of the 21 organic fertilizers that demonstrated net N mineralization (excluding the inorganic NaNO₃ reference), 16 fertilizers could be adequately fit to first-order kinetics. As stated above, alfalfa meal immobilized, and the large pellet 3, pellet 4, and mustard seed meal led to high variability between replications and a bad fit. Pellet 2 was removed, as the model adjusted with a high N0 and very low k to account for the more linear pattern of release (Cabrera & Kissel, 1988; Gordillo & Cabrera, 1997; Table 1). For the remaining fertilizers, pseudo R² values ranged from 0.38 to 0.93, with

pellet 1 and bone meal having the poorest fits due to some variability among reps but also due to the appropriateness of the model to describe the kinetics of these products (Figure 1a). Rate constants of mineralization ranged from 0.02 to 0.37 d⁻¹ and N0 from 9.6 to 109.7 g N kg⁻¹ material. Residual sum of squares analysis determined that the individual fertilizers models were significantly different from a full single model (at p = .01), therefore fertilizers require individual parameters to adequately predict N mineralization.

Six of the 15 poultry litters used in this study could not be fit due to the immobilization observed during the first few weeks of the incubation. In contrast to Hadas et al. (1983) and Gordillo and Cabrera (1997), litters in this study did not fit the two-pool model, likely due to the mineralization patterns described above. Gale et al. (2006) observed no differences in the type of fit or the rate of mineralization for raw broiler litter versus stacked broiler litter in their study (fit two-pool, first-order). The stacked litter in their study was dry stacked (no moisture added) for 84 d but as seen through their research, mineralization of litter N can occur rapidly under ideal water content and temperature. If the mineralization is inhibited during stacking, the easily degradable organic N compounds can stay intact and then have the potential to rapidly mineralize when applied to moist soil. With no direct information for the temperature or moisture conditions during stacking or storage for the Gale et al (2006) study or our study, inferences on the effect of stacking or storage are difficult. However, the variation in the initial characteristics of the litters presented in Table 1, indicate a variety of histories and litter sources prior to the N mineralization experiment. The lack of fit of the two-pool model is likely due to the lower mineralization observed and slower release observed in this study (Figure 1). For the poultry litters that were fit to the first-order equation, the pseudo R² ranged from 0.30 to 0.94. The rate constant of mineralization (k) ranged from 0.005 to 0.19 and N0 values ranged from 8.1 to 44.4 g kg⁻¹ material. The linearity observed for PL7 (Figure 1b), led to a higher N0 and lower k than the other poultry litters. Residual sum of squares analysis indicated significant differences between a full model and the individual poultry litters with at p = 0.01; the pseudo R^2 of the full model of all poultry litters was 0.62.

The composts that could be fit to first-order kinetics showed poor fits with pseudo R² ranging from 0.13 to 0.28. The low mineralization observed by these materials indicates that modeling N release may not be of practical use for producers, still residual sums of squares analysis did determine significant differences between the full model and individual fits observed for the composts.

Parameters N0 and k were simultaneously fit during the regression procedures, but no collinearity was observed between N0 and k. Collinearity between these parameters have been previously observed from fitting N mineralization kinetics (Schomberg et al., 2009; Wang et al., 2003). The

TABLE 2 Regression equations of the relationships determined with initial characteristics, net N mineralized in a 99-d laboratory incubations, and parameters determined from the first-order fit to N mineralization kinetics

Regression equation ^a	Adjusted R ²
Net N mineralized, $\% = -6.19 \times (\text{C/N})$ ratio + 82.2	0.616
N0, g kg ⁻¹ = $0.82 \times (TN, g kg^{-1}) - 16.81$	0.754
Net N mineralized, g kg ⁻¹ material = $0.94 \times (TN, g kg^{-1} material) - 26.54$	0.910
N0, g kg ⁻¹ = $0.82 \times (ON, g kg^{-1}) - 12.22$	0.762
Net N mineralized, g kg ⁻¹ material = $0.93 \times (ON, g kg^{-1}) - 20.95$	0.907
TN, g kg ⁻¹ material = $1.01 \times (ON, g kg^{-1}$ material) + 4.35	0.983

^aN0, pool of mineralizable nitrogen; TN, total nitrogen; ON, organic nitrogen.

measured net N mineralized (g kg⁻¹ dry material) correlated with the fit pool of mineralizable N (N0) with an R² of 0.95 and a slope of 1.1. Using the fit parameters, N0 and k, the modeled versus the measured fit for each product type was determined for the days sampled in this experiment. Fits were good for the fertilizers (Figure 2a), with an R² = 0.92 and a slope near 1 (p < .0001). Poultry litters (Figure 2b) had an R² of 0.74 and a slope near 1 (p < .0001). The intercepts were not significantly different than 0 for either model. The modeled versus measured fit for the composts (Figure 2c) was poor (R² = 0.38) which reflected the poor fits of first-order kinetics and low mineralization observed for the materials.

3.3 | Predicting N mineralization

With the residual sums of squares analysis indicating the need for individual parameters to predict mineralization from fertilizers, poultry litters, and composts, the initial characteristics were regressed against the net N mineralization determined after 99 d, the fit N0 values, and the fit *k* values determined in the long term incubation experiment.

Net N mineralized (expressed as % of organic N applied) was negatively correlated to the C/N ratio of the materials (Table 2; Figure 3). Net mineralization stopped as the C/N ratio approached 11. Removing any materials with a C/N ratio greater than 11, led to an $R^2 = 0.61$ with the model, slope and intercept significant at p < .0001. The negative correlation between the net N mineralized and the C/N ratio has long been known, however, the value and effectiveness of the C/N ratio as a reliable predictor have varied in the literature. Gale et al. (2006) determined similar relationships to our study with plant available nitrogen (initial plus mineralized N) and the C/N ratio of broiler litters, dairy solids, composts, and specialty products, with a "breakeven point" C/N ratio of

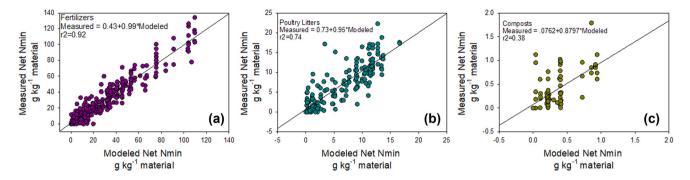


FIGURE 2 Modeled versus measured values for net nitrogen mineralization determined using first-order kinetics for fertilizers, poultry litters, and composts that could be fit to the first-order kinetics mineralization equations. Model parameters *k* (rate constant of mineralization) and N0 (the pool of mineralizable nitrogen) were fit simultaneously during non-linear regression

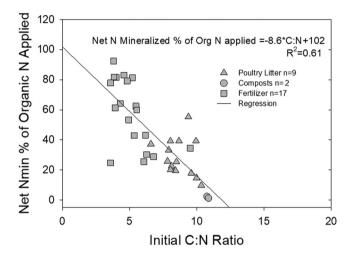
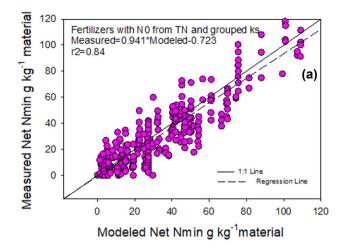


FIGURE 3 The relationship of net nitrogen mineralization after 99-d incubation (as a percent of the organic N applied) with the initial C/N ratio of the fertilizers and materials for materials with a C/N ratio less than 11

15. Sigurnjak et al. (2017) determined a strong relationship between the C to total organic N ratio and mineralization with animal manures and digestate, where materials with a low C to organic N ratio and high NH₄-N exhibited mineralization similarly to inorganic fertilizers. A C/N ratio of 12 has been cited for compost maturity (Bernal et al., 1998) and a C/N ratio of 13 was used for modeling net mineralization from plant residues by Vigil et al. (1991) and Woodruff et al. (2018). In contrast, Franklin et al. (2015) observed mineralization of composts when the C/N ratio was less than 20, and noted the C/N ratio was not an adequate predictor for the composts that showed higher rates of mineralization or lower C/N ratios in their study. Carbon and N quality will contribute to the accuracy of the prediction of the C/N ratio (Flaval & Murphy, 2006), but variations in values cited in the literature could also be attributed to conditions during study incubation (soil particle size, water content and temperature; Gordillo & Cabrera, 1997; Mowrer et al., 2014). Overall, a good relationship was determined in this study with some exceptions like bone meal. Even with a C/N ratio less 4, bone meal showed low mineralization with only 25% N applied becoming available. It is likely in the case of bone meal, carbon and nitrogen quality could explain the lack of fit for this material.

Net Nmin (g kg⁻¹ material) and N0 (g kg⁻¹ material) correlated to both total N (g kg⁻¹ material) and organic N (g kg⁻¹ material) (Table 2, providing easily measureable characteristics to predict mineralizable N. A particularly strong relationship ($R^2 = 0.91$) was determined for net Nmin (g kg⁻¹) with total N and organic N. Gordillo and Cabrera (1997) determined positive correlations with net N mineralization (g N⁻¹ kg litter) and total N similar to ours which explained 83% of the variability observed in their study. For four organic based fertilizers, Stadler et al. (2006) determined that total N of the fertilizers explained 98% of the variability in N mineralization, with similar results regardless of soil texture. With many of the commercially fertilizers containing high N products like feather and blood meal that have been further processed, it is likely that much of the readily mineralizable N is available in the

Similar to results determined for poultry litter by Gordillo and Cabrera (1997), relationships were determined between the measured initial characteristics of the materials and N mineralized and the fit pool of mineralizable N (N0) but not the rate constant of mineralization (k). In terms of predicting N mineralization, accurately fitting the pool of mineralizable N (N0) may be more important than fitting individual k values (Gordillo & Cabrera, 1997; Schomberg et al., 2009). Using a similar approach to Schomberg et al. (2009) and Wang et al. (2003) for soils, a single k was fit by product type and the amount of observed mineralization to create a predictive index that can used for N mineralization from fertilizers and poultry litters. Full models were fit to the first-order model (Equation 2) for each product type (split into sub-groups) with the individual N0 values fixed and a k iterated for each group. The fertilizers were split into two groups, those that



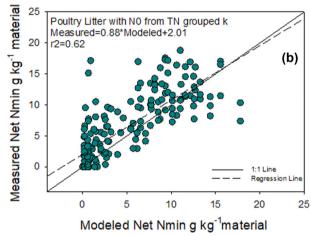


FIGURE 4 Modeled versus measured net N mineralized from the commercial fertilizers (a), poultry litters (b), and composts (c) using a grouped k (rate constant of mineralization) depending on the percent mineralization of the material and a N0 (pool of mineralizable nitrogen) determined from the initial total nitrogen of the material. This approach allows for the prediction of nitrogen mineralization without the use of long-term incubations

mineralized greater than 70% of organic N applied (n = 7) and those mineralized less than 70% of organic N applied (n = 9), with respective fit k values of 0.117 d⁻¹ (pseudo R² = 0.87) and 0.0873 d⁻¹ (pseudo R² = 0.82). For the fertilizers, using the individual N0 values (determined through the incubation) and grouped k values determined by the percentage of mineralization led to an R² of 0.89, a slope of 0.97 and an intercept of 1.62, both significant at p < .001 for a regression between the modeled versus measured values. Unlike the fertilizers, the poultry litters in this experiment did not lend themselves to different groups to fit a rate constants of mineralization, k. Using all the litters, the full model of the poultry litters (set N0 and iterated k) led to a grouped k of 0.0119 d⁻¹ with a R² = 0.44 for the modeled versus measured values.

Due to the ease of measuring only total N, compared to measuring nitrate, ammonium, and total N for organic N determination, the relationship between N0 and total N

was used for predictive capabilities. For both farmers and testing labs, reducing measurements will decrease costs and time. Using the equations for predicting N0 (Table 2, where N0, g kg⁻¹ = $0.818 \times (\text{total N, g kg}^{-1}) - 16.81$, and the grouped k values, the ability to predict net N mineralized was determined by only using the initial total N of the material (Figure 4). For the fertilizers (Figure 4a), these indices predicted net N mineralized with a R² of 0.84, the intercept was not significantly different from zero (p = 0.389) and the slope neared 1 at 0.941 (p < .0001). For the poultry litters (Figure 4b), the measured versus model had a R² of 0.62, an intercept of 2.00 (p < .0001) and a slope of 0.877 (p < .0001).

4 | CONCLUSIONS

A wide range of nitrogen mineralization was observed in the organic fertilizers and materials dependent on the product type and initial characteristics of the material. Many of the commercial fertilizers showed a high percentage of mineralization and rapid release after application. Organic fertilizers are typically referred to as "slow release", but this research has shown that we need to alter the terminology used to describe N release from these products to avoid confusion. Net N mineralized, described by first-order kinetics, could be accurately predicted using a grouped k (by product type) an easily measurable chemical index, total N, to predict the pool of mineralizable N.

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