



## Relationship between soil properties and nitrogen mineralization in undisturbed soil cores from California agroecosystems

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### ABSTRACT

Soil nitrogen (N) mineralization rates from different agricultural regions in California were determined and related to soil properties. Undisturbed soil cores were sampled in spring from 57 fields under annual crop rotations and incubated at 25°C for 10 weeks. Soil properties varied across and within regions, most notably those related to soil organic matter (SOM), with total soil carbon ranging from 6 to 198 g kg<sup>-1</sup>. Multivariate linear regression was used to select soil properties that best predicted N mineralization rates. Regression models with a good fit differed between soils with high and low SOM contents, but generally included a measure of SOM quantity, its quality as well as soil texture or mineralogy. Adjusted R<sup>2</sup> values were 0.95 and 0.60 for high and low SOM soils, respectively. This study has shown that information on soil properties can contribute to better estimates of N mineralization in soils of contrasting characteristics.

### ARTICLE HISTORY

Received 22 July 2018

Revised 16 November 2018

Accepted 20 November 2018

### KEYWORDS

Total soil nitrogen;  
particulate organic matter;  
FDA hydrolysis; soil organic  
matter

## Introduction

Nitrogen (N) use efficiency in intensive cropping systems is often low, which can lead to elevated nitrate (NO<sub>3</sub><sup>-</sup>) concentrations in groundwater (Lassaletta et al. 2014). The highly productive cropping systems in California are no exception. A study focusing on the Tulare Lake Basin and the Salinas Valley found that many wells exceeded maximum NO<sub>3</sub><sup>-</sup> concentration limits for drinking water (Harter et al. 2012). California growers face increasing regulatory pressure to improve N use efficiency in crop production to reduce NO<sub>3</sub><sup>-</sup> leaching. To remain competitive, growers need to improve N use efficiency while maintaining high yield levels. Although computer-based decision support tools have become increasingly popular and sophisticated, less progress has been made to estimate the amount of N made available through net N mineralization during the cropping season. This deficiency is likely a weak component in many of these tools, potentially affecting their accuracy.

Soil N mineralization is affected by climatic factors (Dessureault-Rompré et al. 2010; Guntiñas et al. 2012), soil properties (Ros et al. 2011; Dessureault-Rompré et al. 2015), and crop management (Senwo and Tabatabai 2005; Wade, Horwath, and Burger 2016). With all these factors affecting N mineralization, estimating site-specific mineralization rates is challenging (Vigil et al. 2002; Wade, Horwath, and Burger 2016). This is especially true for California, where many crops are grown on soils with a wide range of

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properties (Johnston 2003; Zinke and Delwiche 1983). Many soil tests to predict N mineralization have been developed over the years (Ros, Temminghoff, and Hoffland 2011). Previous work with agricultural soils from California did not identify a test with a close enough correlation with the N mineralization potential to be used commercially (Geisseler 2005; Wade, Horwath, and Burger 2016), even though some of these tests have been found to be good predictors of N mineralization in other regions (e.g. Franzluebbers et al. 2000; Williams et al. 2007). Currently, no widely applicable and reliable method is available to estimate N mineralization rates for cropping systems in California. While the diversity in soil properties may prevent a single test from being a reliable predictor of N mineralization across different regions in California, it provides an opportunity to investigate the effects of soil properties on N mineralization. The results of such a study may contribute to the development of an approach to estimate the N mineralization potential of agricultural soils in California and other Mediterranean agroecosystems.

Total soil N is often found to be a good predictor of N mineralization (Dessureault-Rompré et al. 2015; Matar et al. 1991). However, compiling data from different studies carried out in the United States and Europe, Vigil et al. (2002) found a very weak correlation between N mineralization and total N as well as soil organic matter (SOM). This finding is consistent with a recent study from California with soils from the Central Valley and Salinas Valley, where Wade, Horwath, and Burger (2016) found that the Pearson correlation coefficient between total N and N mineralized in laboratory incubations conducted for different lengths of time did not exceed 0.57.

Other soil properties, especially SOM pools and fractions have been found to help explain the variability in N mineralization (Ros 2012). These SOM pools include permanganate oxidizable carbon (Weil et al. 2003) and particulate organic matter (POM; Bu et al. 2015), which are considered readily available pools of SOM. Exocellular enzyme assays such as fluorescein diacetate (FDA) hydrolysis are a measure of substrate availability and can provide insight into microbial activity (Green, Stott, and Diack 2006; Schnürer and Rosswall 1982). Furthermore, soil texture and mineralogy are also known to influence SOM turnover due to physical and chemical interactions (Kleber et al. 2015).

Nitrogen mineralization rates are often determined in laboratory incubations (Jarvis et al. 1996; Stanford and Smith 1972). While incubations allow controlling temperature and soil moisture, sample handling, especially sieving and drying may affect N mineralization rates (Cabrera and Kissel 1988, Franzluebbers 1999). This often leads to high initial rates, which decrease over time. In contrast, the amount of N mineralized increases more linearly over time in undisturbed cores (Nordmeyer and Richter 1985). Furthermore, the amount of N mineralized during laboratory incubations may originate from SOM or recently applied organic fertilizer and incorporated crop residues. The variable contribution of these different sources could be a major reason why the proportion of soil N that is mineralized in laboratory studies is so variable. In the present study we minimized these confounding factors by determining N mineralization in undisturbed soil cores from fields with no recent history of manure applications and legume cover crops.

The objectives of this study were (i) to assess the magnitude and range of N mineralization rates from SOM in California soils under annual crop rotations, (ii) to relate N mineralization rates to measured soil properties in order to determine their effect on N mineralization and (iii) to evaluate their usefulness in predictive models. The hypothesis was that total N is the dominant predictor for soil N mineralization independent of the SOM content and that other soil properties, such as texture, pH or electrical conductivity (EC) improve prediction of N mineralization in soils with a low SOM content, but are less relevant in soils with a high SOM content.

## Material and methods

### Soil sampling

A total of 57 field sites, located in the northern half of California were included in this study. The fields were under annual row crops and had no recent history of legume cover crops, manure or

compost applications. Furthermore, sites were selected to represent major soil series in the region. Soils at the sites in the Sacramento-San Joaquin Delta and Tulalake basin were predominantly classified as Mollisols and Histosols (United States Department of Agriculture [USDA] Soil Taxonomy). Mollisols were also most common at the sites in the Salinas Valley. In the Sacramento and northern San Joaquin Valleys, Vertisols, Inceptisols, Entisols and Alfisols were most common, while the southern San Joaquin Valley sites were dominated by Aridisols. In total, the soils belonged to eight soil orders, based on USDA Soil Taxonomy, highlighting the variability in soils under agricultural production in California.

Samples were taken pre-plant in spring 2016 and 2017. At each site, the field was divided into 3 random blocks and separate soil samples were taken from each block. Samples included undisturbed soil cores and a representative sample for these cores for laboratory analyses. Plant residues and the hard, dry surface soil (top 2.5 to 5 cm) were removed before sampling. Below this dry layer, the moisture content of most soils was close to field capacity with the water filled pore space averaging 54%, and only three sandy soils having a water filled pore space below 40% with the lowest value being 31%. Using field moist soils minimizes the burst in microbial activity when water is added for the incubation. Two undisturbed cores were taken per block (6 cores field<sup>-1</sup>) in plastic sleeves with a diameter of 4.5 cm and a length of 15 cm with a core sampler, while representative samples from the same layer were taken with a soil probe from the area surrounding the cores. Foam inserts were placed on top of the cores before capping to minimize disturbance during transport to the lab. The representative samples were placed into plastic bags. All samples were kept on ice in coolers until returning to the laboratory where they were stored in a cold room at 4°C before processing.

### ***Nitrogen mineralization study***

Undisturbed soil cores were weighed and the height measured to determine soil volume, bulk density and porosity. For the incubation, cores were adjusted to 60% water filled pore space or 60% water holding capacity, whichever was lower, to provide optimal moisture conditions for microbial activity and N mineralization (Linn and Doran 1984). Soil moisture in the cores was adjusted by injecting deionized (DI) water with a site-port syringe needle. The cores were then covered with punctured plastic wrap and two cores (treated as subsamples) from each block were placed in an incubator set to 25°C. Core moisture content was monitored weekly and adjusted with the addition of DI water to maintain an optimal moisture content, which was never allowed to drop below 50% water filled pore space or water holding capacity during the incubation. After 10 weeks, the cores were removed from the sleeves, sieved and analyzed for gravimetric moisture content, as well as ammonium-N ( $\text{NH}_4^+$ -N) and  $\text{NO}_3^-$ -N concentrations as described below. Net N mineralization was calculated by subtracting the initial mineral N (sum of  $\text{NH}_4^+$ -N and  $\text{NO}_3^-$ -N) in the representative samples from the final mineral N concentration in the cores.

### ***Soil analyses***

Representative samples were initially sieved to 4.75 mm and analyzed for gravimetric moisture content by drying them at 105°C for 24 h. Ammonium-N and  $\text{NO}_3^-$ -N were determined on field-moist samples, while soils for the other analyses were first air-dried at room temperature, with subsamples being sieved to 2 mm when necessary.

Soil water holding capacity was determined by adding approximately 30 g of air-dried soil, sieved to 4.75 mm, into funnels containing Fisherbrand Q5 filter paper. The funnels were then placed on beakers filled with DI water, such that the tip of the filter paper was submerged. Soils were allowed to imbibe water until the surface began to glisten at which point they were removed and dried at 105°C to determine the moisture content, which corresponded to 100% water holding capacity.

To measure soil  $\text{NH}_4^+$ -N and  $\text{NO}_3^-$ -N concentrations, 6 g of field-moist soil were extracted with 30 mL of 0.5 M  $\text{K}_2\text{SO}_4$  (Mulvaney 1996). Samples were shaken for 1 h on a reciprocal shaker and

filtered through Fisherbrand Q5 filter paper. Extracts were analyzed for both  $\text{NH}_4^+\text{-N}$  and  $\text{NO}_3^-\text{-N}$  colorimetrically with a Shimadzu UV1820 Spectrophotometer at wavelengths of 650 nm and 540 nm, respectively. Ammonium-N was measured with the Berthelot reaction (Forster 1995; Verdouw, van Echteld, and Dekkers 1978), while  $\text{NO}_3^-\text{-N}$  was measured with a vanadium (III) reagent (Doane and Horwath 2003).

Total carbon (C) and N were determined by dry combustion on a Costech Elemental Combustion System (ECS 4010; Nelson and Sommers 1996). Soils were tested for the presence of carbonates by applying a few drops of hydrochloric acid to the samples. No significant amounts of carbonates were detected. Particulate organic matter C (POC) and N (PON) were determined using the procedure described by Cambardella and Elliott (1992). Ten grams of air-dried soil, sieved to 2 mm, were dispersed in 30 mL of a 5% sodium (Na) hexametaphosphate solution by shaking the samples on a reciprocal shaker for 15 h. Afterwards, the slurry was quantitatively transferred to a 53- $\mu\text{m}$  sieve and washed with DI water to remove silt and clay-sized particles. Sand-sized particles were then dried at 60°C and analyzed for total C and N. The method used to determine permanganate oxidizable C, which has been proposed as a measure of biologically active soil C, was based on Weil et al. (2003) with modifications proposed by Culman et al. (2012). For each replicate, two subsamples of 2.5 g of air-dried soil, sieved to 2 mm, were used. The amount of soil was reduced to 1 g for sites with a high SOM content. The extracts were analyzed colorimetrically on a Shimadzu UV1820 Spectrophotometer at a wavelength of 550 nm.

To assess general enzyme activity in soil samples, FDA hydrolysis was measured. The approach used was based on Green, Stott, and Diack (2006) and Prosser, Speir, and Stott (2011) with slight modifications. Three subsamples of 1 g of air-dried soil, sieved to 2 mm, were weighed into 50-mL centrifuge tubes and 30 mL of tris(hydroxymethyl)aminomethane (THAM) buffer (pH 7.6) was added. This was followed by an addition of 0.30 mL of FDA solution to 2 subsamples and acetone to 1 subsample, which served as the control. Samples were shaken for 3 h on a reciprocal shaker at room temperature. After shaking, 1.2 mL of acetone was added to each sample and the slurries were mixed on a vortex to stop the reaction. Samples were then let to rest for 10 minutes before 1.5 mL of supernatant was pipetted into 1.5-mL centrifuge tubes, which were then centrifuged at 8745 G for 5 minutes. The samples were then transferred to cuvettes and read on a Shimadzu UV1820 Spectrophotometer at a wavelength of 490 nm.

Two pools of iron (Fe) were analyzed, namely pyrophosphate-extractable Fe and citrate-dithionite-extractable Fe. The extraction procedure for pyrophosphate-extractable Fe was adapted from McKeague (1967), while the method for dithionite-extractable Fe was adapted from Mehra and Jackson (1958) and Holmgren (1967). A 0.4-g sample of air-dried soil sieved to 2 mm was shaken for 16 h with either 40 mL of 0.1 M Na pyrophosphate or 40 mL of 0.3 M Na citrate plus 0.4 g of Na dithionite. Samples were then allowed to rest for 24 h, after which a 1.5-mL aliquot was centrifuged at 15,600 G for 30 minutes and 4,000 G for 10 minutes, respectively. The extracts were analyzed colorimetrically (Dominik and Kaupenjohann 2000). Pyrophosphate extracts of soils with a high SOM content were diluted 10-fold, while all citrate-dithionite extracts were diluted 20-fold. Samples were read on a Shimadzu UV1820 Spectrophotometer at a wavelength of 565 nm.

A 2:1 DI water:soil suspension (by weight) was used to determine soil EC and pH. Samples were shaken on a reciprocal shaker for 15 minutes and allowed to stand for 1 h before EC and pH were measured in the supernatant with a Fisher Scientific Digital Meter 09-326-2 and an Orion Model 250A, respectively. Particle size analysis was conducted using the pipet method (Soil Survey Staff 2014).

### **Statistical analyses**

Statistical analyses were done using the SAS software system, version 9.4 (SAS Institute, Inc. 2013). Multiple linear regression was performed using the 'REG' procedure. The models were grouped based on the number of variables included and within each group arranged based on Mallows' Cp.

Model selection was also based on Mallows' Cp. Principal component analysis (PCA) was done using the 'FACTOR' procedure.

## Results

### Soil properties

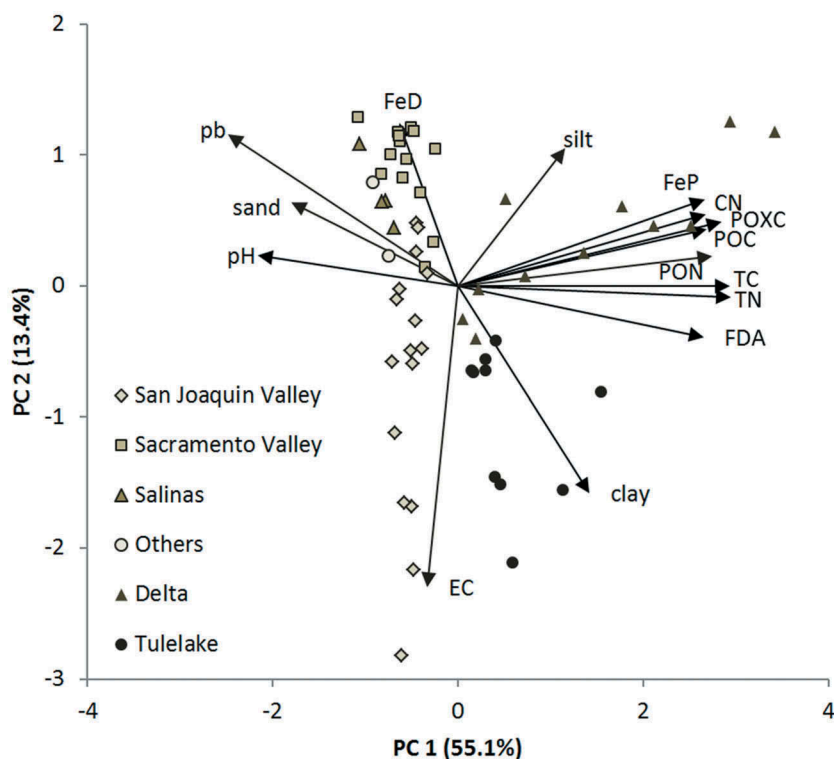
The soil properties included in our analysis varied considerably across sites (Table 1). Most pronounced were the differences in properties related to SOM content. Soil from the Delta and the Tulalake basin had the highest total C contents ranging from 33 to 198 g kg<sup>-1</sup>. Total C was much lower and less variable in the soils from the Sacramento, San Joaquin and Salinas valleys, ranging from 6 to 15.3 g kg<sup>-1</sup>. Two soils collected in an area adjacent to the Tulalake basin (labeled as "others" in the tables and figures) had similarly low total C contents. Other soil properties related to SOM content, such as POM, permanganate oxidizable C, pyrophosphate extractable Fe, and FDA hydrolysis followed a similar trend, while bulk densities were lower in soils with a high SOM content.

Across all sites, pH ranged from 5.6 to 8.1 and EC from 8 to 250 mS m<sup>-1</sup>. Electrical conductivity was especially high in some soils from the San Joaquin Valley (Table 1). The soils also represented a wide range of textures, with the variability within a region generally being larger than across regions. The one exception was the two "other" soils from the Tulalake area which were the sandiest soils in the dataset.

A PCA provided a good overview of the data structure across sites (Figure 1). Principal component (PC) 1 explained 55% of the variability while PC 2 explained 13%. Soil properties related

**Table 1.** Properties of the soils included in the study grouped by region. Values are averages with range in parentheses. For abbreviations, see Table 3.

Soil property	Region					
	San Joaquin Valley	Sacramento Valley	Salinas Valley	Delta	Tulalake	Others
Number of sites	16	14	4	11	10	2
Bulk density (g cm <sup>-3</sup> )	1.19 (1.1–1.31)	1.28 (1.17–1.48)	1.45 (1.32–1.68)	0.84 (0.63–1.33)	0.71 (0.43–0.92)	1.36 (1.34–1.37)
Total C (g kg <sup>-1</sup> )	10.1 (7.3–12.8)	11.1 (6–15.3)	9.2 (6.7–12)	90.4 (33–198.4)	49.8 (31.4–78.6)	7.4 (6–8.8)
Total N (g kg <sup>-1</sup> )	1.16 (0.85–1.41)	1.18 (0.69–1.56)	1.12 (0.83–1.39)	6.22 (2.71–12.48)	4.65 (2.92–7.16)	0.71 (0.65–0.77)
PON (g kg <sup>-1</sup> )	0.14 (0.05–0.21)	0.16 (0.08–0.28)	0.09 (0.05–0.12)	1.62 (0.15–5.25)	0.89 (0.35–1.91)	0.15 (0.12–0.19)
POC (g kg <sup>-1</sup> )	1.72 (0.78–2.55)	1.85 (1.01–3.1)	1.09 (0.56–1.76)	27.41 (2.32–90.87)	10.70 (4.64–25.13)	2.86 (1.8–3.93)
pH	7.58 (7.17–8.06)	7.68 (7.2–8.08)	7.46 (7.24–7.65)	6.54 (5.9–7.27)	7.07 (6.19–7.65)	6.54 (5.57–7.5)
EC (mS m <sup>-1</sup> )	90.3 (14.4–250)	15.2 (7.8–27.8)	20.0 (12.3–24.3)	29.4 (12.9–63)	42.1 (14.3–97.2)	12.3 (11.7–12.8)
Sand (%)	23.0 (8.7–35)	26.4 (5.5–64.9)	46.8 (38.5–60.3)	9.6 (0.9–18.9)	7.6 (2.3–16.1)	83.2 (80.2–86.1)
Silt (%)	40.3 (22.7–56.7)	44.1 (24.1–57.7)	37.2 (27.3–42.9)	47.3 (34.5–60.1)	36.2 (24.2–44.8)	8.2 (5.4–11.0)
Clay (%)	36.6 (20–49.2)	29.4 (10.9–58.8)	16.0 (11.9–21.5)	43.1 (32.2–61.5)	56.2 (49.4–68.6)	8.6 (8.4–8.8)
POXC (mg kg <sup>-1</sup> )	345 (259–477)	369 (262–460)	333 (210–477)	1966 (775–3578)	776 (245–1564)	217 (192–241)
FDA hydrolysis (mg kg <sup>-1</sup> h <sup>-1</sup> )	16.8 (9.8–30)	14.8 (4.8–33.6)	7.5 (3.4–10.3)	40.1 (25.1–68.8)	34.0 (20.4–76.7)	9.3 (9.1–9.5)
FeP (mg kg <sup>-1</sup> )	88 (34–154)	168 (101–276)	173 (136–261)	4236 (832–7623)	546 (179–2076)	135 (56–215)
FeD (g kg <sup>-1</sup> )	10.80 (7.75–13.46)	14.64 (10.42–17.65)	7.18 (6.32–8.16)	9.77 (7.39–12.32)	3.14 (2.54–4.17)	2.63 (2.25–3.01)



**Figure 1.** Biplot of the PCA for different soil properties of California soils under annual crops included in this study. For abbreviations, see Table 3.

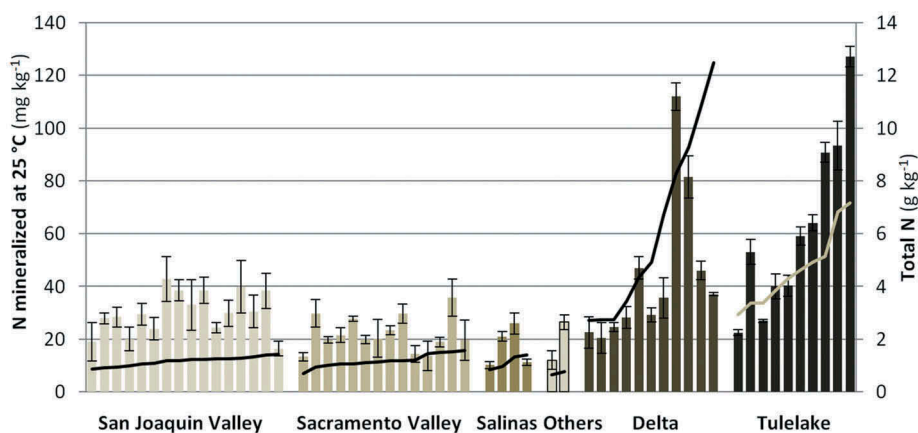
to SOM content as well as pH and bulk density were closely associated with PC 1, while EC, dithionite extractable Fe and to a lesser degree soil texture were related to PC 2. Principal component analysis also revealed a high degree of collinearity among the soil properties associated with SOM content. Soils with a high SOM content from the Delta and Tulelake basin were clearly separated from the soils collected in the other regions along PC 1. The soils with a low SOM content were mainly spread out along PC 2, with the soils from the San Joaquin Valley contributing most of the variability, most likely due to their wide range in EC.

### Nitrogen mineralization rates

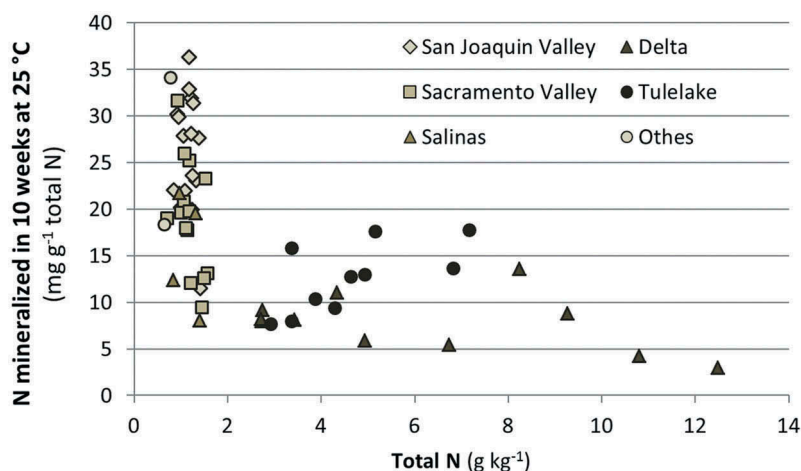
During the 10-week incubation, N mineralization rates in undisturbed soil cores differed considerably across and within regions, ranging from 10 to 127 mg kg<sup>-1</sup> soil (Figure 2). This was especially true for soils from the Delta and Tulelake basin. In contrast, N mineralization was more uniform across soils with a low SOM content. However, within this group, the highest N mineralization rate was more than four times greater than the lowest. With the exception of the Tulelake basin soils, N mineralization was poorly related to total N within each region.

When expressing N mineralization as a fraction of the total soil N, the variability across regions followed a different pattern (Figure 3). The fraction of total N mineralized varied widely across low SOM soils, ranging from 7 to 37 mg g<sup>-1</sup>, with no clear trends across regions. In contrast, the fraction of total N mineralized was less variable in soils with a high SOM content. However, even in these soils, the range was wide, suggesting that total N alone is not a good predictor of N mineralization in agricultural soils in California.





**Figure 2.** Nitrogen mineralization in undisturbed soil cores. The cores were incubated at optimal moisture content at 25°C for 10 weeks. Within the regions the sites are arranged in order of increasing total soil N (solid lines). Error bars represent standard error ( $n = 3$ ).



**Figure 3.** Correlation between total soil N and N mineralization rate in undisturbed soil cores.

### **Correlation between soil properties and N mineralization**

Across all sites, FDA hydrolysis and bulk density were best correlated with N mineralization (Table 2). The correlation was positive for FDA hydrolysis and negative for bulk density. Both soil properties were also well correlated with N mineralization when the dataset was split into two groups based on their SOM contents (Table 2). One group consisted of soils from the Delta and Tulelake basin with a total C content of more than  $31 \text{ g kg}^{-1}$  ( $n = 21$ ), while soils from the other regions, which had a SOM content below  $16 \text{ g kg}^{-1}$  ( $n = 36$ ), were included in the other group. These two groups will be referred to as high SOM soils and low SOM soils, respectively. In contrast, the correlations between N mineralization and total C and N were weaker (and non-significant) in the two groups than across all sites. The squared values for total C and N were less well correlated with N mineralization than the untransformed values. Squared values for total C and N were included because total C and N had a quadratic relationship with POC and PON, respectively (see below). The

**Table 2.** Pearson correlation coefficients between nitrogen mineralization and soil properties. For abbreviations, see Table 3. Significant variables with an  $r > 0.5$  are highlighted.

	All sites		High SOM soils		Low SOM soils	
	r	p	r	p	r	p
TC	<b>0.53986</b>	<b>&lt;.0001</b>	0.25145	0.2715	0.18301	0.2854
TC <sup>2</sup>	0.34905	0.0078	0.11151	0.6304	0.12147	0.4804
TN	<b>0.64869</b>	<b>&lt;.0001</b>	0.42915	0.0522	0.2422	0.1547
TN <sup>2</sup>	<b>0.51526</b>	<b>&lt;.0001</b>	0.29179	0.1993	0.19435	0.256
CN	0.36149	0.0057	−0.16385	0.4779	−0.02189	0.8991
POC	0.39183	0.0026	0.13800	0.5508	0.28848	0.088
PON	0.48161	0.0001	0.24056	0.2935	0.35082	0.0359
POXC	0.49257	<.0001	0.20325	0.3769	0.24249	0.1542
FDA	<b>0.71227</b>	<b>&lt;.0001</b>	<b>0.52695</b>	<b>0.0141</b>	<b>0.61966</b>	<b>&lt;.0001</b>
FeP	0.42532	0.001	0.16931	0.4632	−0.46573	0.0042
FeD	−0.34612	0.0084	−0.16355	0.4787	0.10898	0.5269
pb	<b>−0.75028</b>	<b>&lt;.0001</b>	<b>−0.68478</b>	<b>0.0006</b>	<b>−0.61948</b>	<b>&lt;.0001</b>
pH	−0.37994	0.0036	−0.14062	0.5432	0.1627	0.3431
EC	0.17246	0.1996	0.49843	0.0215	0.48888	0.0025
sand	−0.45096	0.0004	<b>−0.57256</b>	<b>0.0067</b>	−0.26326	0.1208
silt	0.19667	0.1426	0.27108	0.2346	0.12023	0.4849
clay	0.42234	0.0011	0.04878	0.8337	0.28669	0.09

correlation between particle size fractions and N mineralization was not significant, except for a negative correlation with sand content in soils with a high SOM content.

Multiple linear regression was performed with the entire set of soil properties measured (Table 3). Including all sites in the analysis revealed that soils with a high SOM content from the Delta and Tulalake basin had a dominant effect on the regression and that the soils with a low SOM content as a group did not fit the model very well (data not shown). For this reason, the dataset was split into a group of soils with a high SOM content and a low SOM group, as described above.

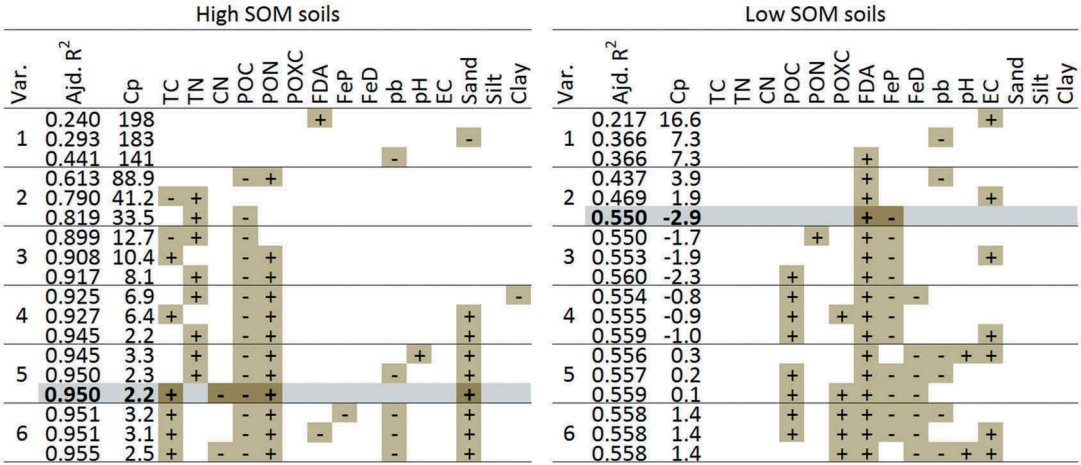
Figure 4 shows the set of soil properties included in regression models with one to six predictor variables. For each group, the best three models based on Mallows' Cp are shown. In soils with a high SOM content, the best models with four to six variables most commonly included POC, PON, sand and either total C or N. In these models, the terms for total N, PON and sand were positive when included in a model, while the term for POC was negative. In these soils, the adjusted R<sup>2</sup> reached 0.945 in the best model with four variables and increased only slightly when additional variables were included. The best model included five variables and had an adjusted R<sup>2</sup> of 0.95 (Equation 1, Figure 5; for abbreviations and units, see Table 3).

$$N_{min} = 20.52 + 2.19TC - 7.20CN + 1.44sand - 9.88POC + 117PON \quad (1)$$

**Table 3.** List of soil properties measured, their units and abbreviations as used in tables, figures and equations.

Soil property	Abbreviation	Unit
Nitrogen mineralization rate	N <sub>min</sub>	mg kg <sup>−1</sup> soil 10 weeks <sup>−1</sup>
Total carbon	TC	g kg <sup>−1</sup> soil
Total nitrogen	TN	g kg <sup>−1</sup> soil
Soil carbon to nitrogen ratio	CN	g g <sup>−1</sup>
Particulate organic carbon	POC	g kg <sup>−1</sup> soil
Particulate organic nitrogen	PON	g kg <sup>−1</sup> soil
Permanganate oxidizable carbon	POXC	mg kg <sup>−1</sup> soil
Fluorescein diacetate hydrolysis	FDA	mg kg <sup>−1</sup> soil h <sup>−1</sup>
Pyrophosphate extractable iron	FeP	mg kg <sup>−1</sup> soil
Dithionite extractable iron	FeD	g kg <sup>−1</sup> soil
Bulk density	pb	g cm <sup>−3</sup>
Electrical conductivity	EC	mS m <sup>−1</sup>
Sand, silt, clay	sand, silt, clay	%
pH	pH	−log <sub>10</sub> (aH <sup>+</sup> )





**Figure 4.** Variables included in multiple linear regression models for soils with high (left panel) and low (right panel) SOM contents. Shown are the three best models based on Mallows' Cp for each step from one to six variables. The highlighted models are the best overall models for each group. The signs indicate whether the correlation between the factor and N mineralization was positive or negative. For abbreviations, see Table 3.

Many of the top models for soils with a low SOM content with two to six variables included FDA hydrolysis and pyrophosphate extractable Fe (Figure 4). While the term for FDA hydrolysis was always positive, the term for pyrophosphate extractable Fe was negative. Less frequently included were POC, dithionite extractable Fe and permanganate oxidizable C. Total C and N were not included in any of these models. In soils with a low SOM content, the best overall model had two variables and reached an adjusted R<sup>2</sup> of 0.55 (Equation 2; Figure 5; for abbreviations and units, see Table 3), which was considerably lower than the best model for soils with a high SOM content. Improvements in the adjusted R<sup>2</sup> were small (< 0.01) when more than two variables were included.

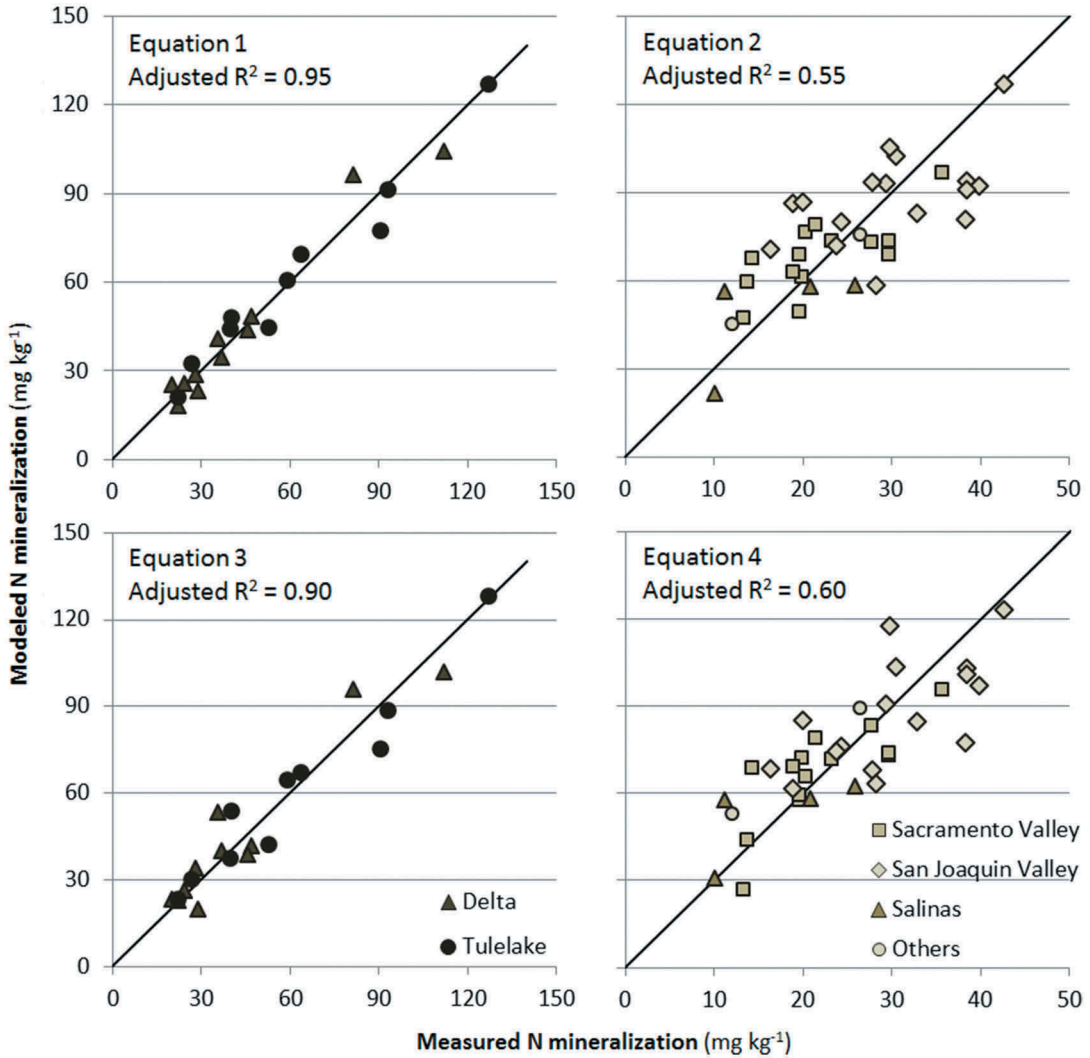
$$N_{min} = 20.42 + 0.861FDA - 0.062FeP \tag{2}$$

While all soil properties associated with SOM were well correlated (Figure 1), the correlations between total C and POC, as well as between total N and PON were especially strong (Figure 6). The increase in PON with increasing total N content was quadratic. In soils with a low total N content, PON contents tended to be lower, accounting for less than 25% of total N. In contrast, in soils with a high SOM content, PON accounted for up to 42% of total N. The relationship between POC and total C followed the same pattern (data not shown). These quadratic relationships suggest that POC and PON might be replaced by exponential terms of total C and N, respectively.

To test these hypotheses, total N<sup>2</sup> and total C<sup>2</sup> as well as total N<sup>4</sup> and total C<sup>4</sup> were included in the dataset, while PON and POC were excluded. For soils with a high SOM content, the best model again included five variables with several of the new terms being included, as was sand content and FDA hydrolysis (Equation 3; for abbreviations and units, see Table 3). However, the adjusted R<sup>2</sup> was lower than when PON and POC were included, reaching only 0.90 (Figure 5).

$$N_{min} = 3.05 + 4.73TN^2 - 0.012TC^2 - 0.007TN^4 + 0.946sand - 0.599FDA \tag{3}$$

In contrast, the changes improved the predictability of N mineralization for soils with a low SOM content. Even though the univariate correlation between N mineralization and total C as well as total C<sup>2</sup> was weak (Table 2), the best model included these two variables, together with silt content and FDA hydrolysis (Equation 4; for abbreviations and units, see Table 3). With these changes, the adjusted R<sup>2</sup> increased to 0.604 (Figure 6).



**Figure 5.** Best fit multiple variable model based on Mallows' Cp for high SOM soils (left) and low SOM soils (right). For model equations see text.

$$N_{min} = -44.82 + 12.79TC - 0.610TC^2 - 0.259silt + 1.123FDA \quad (4)$$

## Discussion

An objective of this study was to relate N mineralization rates to measured soil properties, using multivariate linear modeling. The set of soil properties included in models with a good fit differed between soils with a high and low SOM content. A first indication for the differences between these two groups of soils was provided by a PCA. Low SOM soils varied mainly along an axis associated with EC, soil texture and bulk density, while high SOM soils were also strongly influenced by soil properties that are related to SOM. Many of the measured soil properties associated with SOM have a high degree of collinearity which is reflected in the modelling results that produced numerous models of a similar fit. While this finding suggests that fewer soil properties are needed than measured in this study for a good predictive model, the reoccurrence of specific variables across

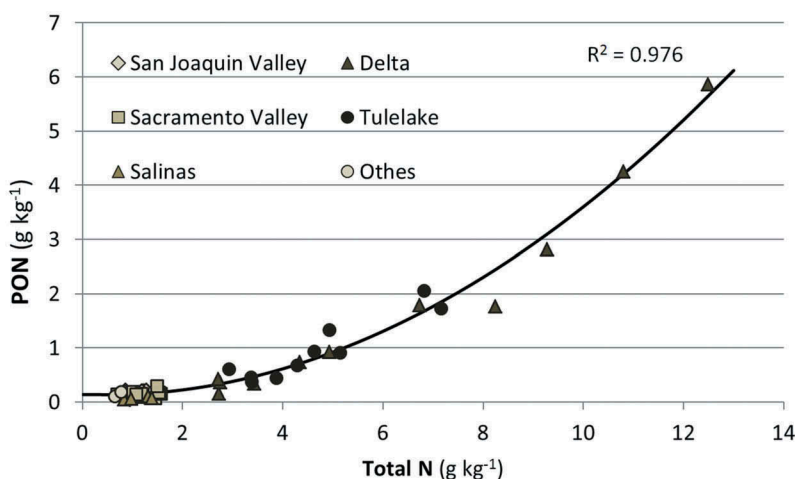


Figure 6. Correlation between total soil N and PON.

models also suggests that some variables potentially have a greater influence on N mineralization than others.

### Soils with a high SOM content

The results of the PCA were confirmed in multivariate models. In the best models with one to six predictor variables for high SOM soils, the quantity (e.g. total C or N) and quality of SOM (often POM), as well as sand content were commonly included variables. This is in agreement with a re-analysis of published data which showed that the size of the SOM pool and its fractions are the most important predictors of N mineralization (Ros 2012). Mirroring SOM contents, both magnitude and variation in N mineralization rates were larger among high SOM soils compared to low SOM soils. Other studies have demonstrated the ability for high SOM soils to mineralize large quantities of N through a growing season, especially upon drainage (Espe et al. 2015; Hacin, Čop, and Mahne 2001; Renger et al. 2002). While N mineralization increased with increasing total N content in our study, the relationship was not linear, especially in the soils from the Delta. These soils showed a parabolic relationship like that observed by Espe et al. (2015) in the same region.

Particulate organic C and N were also important variables in many of the models for high SOM soils. Most commonly, POM is considered a labile pool of SOM and an important source of N and other nutrients (Besnard et al. 1996; Haynes 2005). In fact, several studies have found that POM is positively related to N mineralization (Bu et al. 2015; Kader et al. 2010). In the current study, while the correlation with PON was positive, POC was negatively correlated with N mineralization. The inclusion of the terms for POC and PON in Equation 1 ( $117 \times \text{PON} - 9.88 \times \text{POC}$ ) resulted in an increasingly negative effect of POM on N mineralization with increasing total N content due to the relatively wide C to N ratio of POM, which ranged from 11 to 18. This result and the observation that the POM content increased exponentially with increasing SOM content in these soils, while the proportion of N mineralized decreased, suggest that POM may not be a readily available pool in high SOM soils that formed under anaerobic conditions. The close correlation between SOM and POM in these soils further suggests that POM may be a relatively stable pool of SOM that does not respond strongly to crop management. If this hypothesis is confirmed, e.g. by analyzing samples from the same site over several cropping seasons, then POM would not need to be measured annually to determine the N mineralization potential of the soils in the Delta and Tulelake basin.

In the re-analysis of published data mentioned above, SOM quality was not an important predictor of N mineralization (Ros 2012), which seems to contradict our finding. However, in their analysis, quality referred to C to N ratio and extractable organic fractions expressed in percent of total C or N, while POM was not included in the analysis. In contrast to their findings, the C to N ratio of SOM was included in some of our models with a good fit.

A third variable that was commonly included in models was sand content. Soil texture has often been linked to N mineralization. Interestingly, Ros et al. (2011) found increased N mineralization in sandier soils relative to clayey soils, while Kader et al. (2010) reported a significant negative correlation between N mineralization and sand content, though these authors stated that their studied soils differed little in such properties. In our dataset, the correlation between sand content and N mineralization was negative in a univariate analysis, while it was positive in multivariate models. A possible explanation for this finding is that there was a negative correlation between sand content and total N in these soils ( $r = -0.57$ ;  $p = 0.006$ ), hence the negative univariate correlation. When combined with a measure of SOM quantity, the positive effect of sand content may be due to the fact that sand does not protect SOM, making it more accessible for decomposition (Jarvis et al. 1996). However, increasing sand content may also result in an increased POM content, which as discussed above, had a negative effect on N mineralization. In a study with wetland soils, Sleutel et al. (2008) found that bulk density and clay content were good predictors of N mineralization. They attributed this finding to the effect of these soil properties on pore structure. In our study, bulk density increased with sand content and both properties were negatively correlated with SOM content and N mineralization, though the former to a greater degree. The PCA also revealed that sand content and bulk density were closely related. It is therefore possible that sand content and bulk density had an effect on pore structure, which in turn influenced N mineralization in our soils with a high SOM content. In these soils, sand content seems to provide more information than bulk density or clay content in models that also include SOM characteristics.

### **Soils with a low SOM content**

Across all sites, the N mineralization rates in low SOM soils were comparable to other work conducted on soils from the San Joaquin and Sacramento valleys (Wade, Horwath, and Burger 2016) and from other regions of Mediterranean climate (Matar et al. 1991). In our low SOM soils, pyrophosphate extractable Fe and FDA hydrolysis were important variables in many models. The rate of FDA hydrolysis is a measure of general enzyme activity in soil, and is thus related to SOM availability and quality. Therefore, in both groups of soils, the prediction of N mineralization was best when a measure of SOM quality was included. While POM was an important predictor of N mineralization in high SOM soils, FDA hydrolysis was important in low SOM soils.

Pyrophosphate extractable Fe represents Fe associated with SOM. Polyvalent Fe ions are known to interact strongly with SOM (Stevenson 1994) and contribute to chemical stabilization (Kleber et al. 2015). In fact, the term for pyrophosphate extractable Fe was negative in all models, suggesting that increasing contents reduced N mineralization. Kader et al. (2010) also found pyrophosphate extractable Fe to be negatively associated with N mineralization while Wade et al. (2018) found that poorly crystalline Fe oxides ( $\text{NH}_4^+$ -oxalate extractable Fe) was a better predictor of N mineralization than pyrophosphate extractable Fe. Both Fe fractions had negative or positive effects, depending on the duration of the incubation (Wade et al. 2018).

Many studies have reported a close correlation between total N and N mineralization (Schomberg et al. 2009; Sharifi et al. 2007; Wade, Horwath, and Burger 2016). In contrast to our hypothesis, this was not the case in our soils with a low SOM content. In these soils, the correlation was weak and the proportion of total N mineralized varied greatly, ranging from 0.7 to 3.7%. This is in line with Kader et al. (2010) who reported a non-significant relationship between total N and N mineralization and a similar range of 0.8–5.0% of total N mineralized in soils with a comparable total N content. However, our model for low SOM soils could be

improved when the squared total C was included as a negative term in combination with total C, silt content and FDA hydrolysis. While soil texture was not included as a variable in many models with a good fit, particle size distribution will likely have a more pronounced effect on N mineralization in the field, as soil texture greatly affects water holding capacity and drainage. In our study, N mineralization was determined in cores with a constant moisture content. In the field, sandy soils dry much faster than clay-rich soils after a rainfall or irrigation event, and reach conditions under which microbial activity is reduced faster than clay-rich soils. However, sandier soils tend to warm up faster in spring than clay-rich soils, which may increase microbial activity. Therefore, the effect of soil texture on N mineralization likely depends on environmental conditions.

Even though EC was an important variable separating the soil with a low SOM content in the PCA, it was not a dominant variable in multivariate models, suggesting that within the range observed, EC did not affect microbial activity strongly. In soils with a low SOM content, the measured soil properties were less well correlated with N mineralization and total N was a less important factor than in soils with a high SOM content (Figure 4). Furthermore, our models based on chemical soil properties did not considerably improve prediction of N mineralization in Central Valley soils compared to soil N mineralization tests investigated in previous studies (Geisseler 2005; Wade, Horwath, and Burger 2016). The difficulty to predict N mineralization based on soil tests or soil properties may be due to the large variability of cropping systems and crops grown in the Central Valley. The results of this study and previous work suggest that soil properties and soil tests cannot fully capture the effects of crop management. For example, Wade, Horwath, and Burger (2016) found that prediction of N mineralization could be improved by grouping the soils based on their cover crop history. The sites included in the present study had no recent history of cover cropping, suggesting that other management related factors may need to be taken into account as well. In soils with a low SOM content, crop residues and residue management may be important factors affecting N mineralization rates. Despite the fact that the previous crops were harvested at least six months before soils were sampled, partially decomposed crop residues may still have had an effect on N mineralization. With low SOM contents, residues comprise a larger proportion of the bioavailable organic material and they are more variable than highly decomposed SOM. Furthermore, FDA hydrolysis, which was an important variable in models for soils with a low SOM content, has been shown to be linked to cropping history and residue management (Vinther, Hansen, and Olesen 2004; Wegner et al. 2015). Therefore, information on residue characteristics and management may need to be combined with soil properties or soil tests for robust estimates of N mineralization in these soils with a low SOM content.

## Conclusions

Nitrogen mineralization in soils under annual crops differed widely across agricultural regions in California. Dividing the soils into two groups based on their SOM content improved prediction of N mineralization based on soil properties. In contrast to other studies, total N alone was not a very accurate predictor of N mineralization. Even though many of the measured soil properties associated with SOM had a high degree of collinearity, models for both groups consistently included a measure of SOM content and quality, as well as texture or mineralogy. These findings show that although SOM content is important, other factors can exhibit strong influence on N mineralization and need to be included in models. Furthermore, high levels of collinearity mean that several multivariate models have a good fit, which allows selecting a model that includes soil analyses that are less labor intensive and more suitable for soil test labs. While predicting N mineralization in high SOM soils was very successful, models describing low SOM soils would likely benefit from the inclusion of crop residue characteristics and management. Agricultural soils in California cover a wide range of soil properties. This study has shown that information on soil properties can contribute to better

estimates of N mineralization in soils of contrasting characteristics. The results of this study are an important step towards the development of decision support tools that aid growers in refining N fertilizer budgets and reduce environmental and economic costs associated with low N use efficiency.

## Acknowledgments

This work was supported by the California Institute for Water Resources and by startup funding provided to Daniel Geisseler. We would like to thank Irfan Ainuddin, Kelley Liang and Patricia Lazicki for help with soil sampling and lab analyses.

## Funding

This work was supported by the California Institute for Water Resources

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