Estimating Available Nitrogen in Central Valley Soils

By

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Abstract

Predicting nitrogen mineralization has been the focus of many agricultural researchers for decades. This project was designed to investigate the soil properties that influence potential nitrogen mineralization in the northern Central Valley of California. A total of seventeen sites featuring annual cropping systems with a variety of common crops such as corn (*Zea mays*), watermelon (*Citrullus lanatas*), safflower (*Carthamus tinctorius*), sunflower (*Helianthus annuus*), sorghum (*Sorghum bicolor*), processing tomatoes (*Solanum lycopersicum*), and cotton (*Gossypium hirsutum*) were included, spanning from Colusa to Tulare Counties. We studied nitrogen mineralization using both field trials as well as laboratory incubations of undisturbed soil cores, in conjunction with continuous soil sampling of those sites every 5-6 weeks throughout the growing season to capture seasonal nitrogen turnover. Those soils were characterized and the results statistically analyzed, and a model was developed that determined particulate organic nitrogen and silt content as the best predictors of nitrogen mineralization in the undisturbed soil cores (adjusted-$R^2 = 0.65$, $P < 0.05$). Over 70% of the variability in seasonal nitrogen mineralization at optimal soil moisture was described by only particulate organic nitrogen, while soil moisture was confirmed as a major controlling variable in determining nitrogen mineralization. Furthermore, even at the lowest soil moisture contents, nitrogen mineralization continued.

Two separate smaller studies were also performed to determine crop residue effects on nitrogen availability. One included a field trial using seven different crop residues followed by a laboratory incubation of undisturbed soil cores, and the other included a laboratory incubation with two different residues at varying residue and soil moisture content.

Seven different common crop residues (namely corn (*Zea mays*), watermelon (*Citrullus lanatas*), safflower (*Carthamus tinctorius*), sunflower (*Helianthus annuus*), sorghum (*Sorghum bicolor*), processing tomatoes (*Solanum lycopersicum*), and cotton (*Gossypium hirsutum*) were incorporated in the field trial. By the end of the incubation, cotton residues resulted in the greatest increase in soil mineral N, and sunflower residues resulted in the greatest nitrogen immobilization when compared to the control without residue. The difference between the two treatments was 13.7 mg N kg^{-1} OD soil, or approximately 28.4 kg N ha^{-1} in the top 15 cm of the soil.

Finally, we performed two 10-week laboratory incubations investigating soil and residue moisture's effect on nitrogen mineralization using processing tomato and broccoli residues. At the beginning of both incubations, residue moisture had a significant effect on nitrogen mineralization, however, by the end of both incubations, residue moisture was no longer significant, while soil moisture became increasingly important ($P < 0.05$). During the 10-week incubation, 21.6% and 50% of the total nitrogen in tomato and broccoli residues was mineralized, respectively. Differences are likely due to the residue's carbon:nitrogen ratios and lignin content. The results of these studies will be used by growers in the region to improve upon their fertilizer management practices and make informed decisions based on cropping history and soil properties.

Land Acknowledgement

I would like to acknowledge the ancestral homelands of the California Patwin, Yokuts, and Nisenan Tribes who have continued to manage and steward this land for thousands of years. I dedicate this labor and research to your past, present, and future generations. It's been a gift to work with the soil you have tended to, and to feel your presence in the land we currently occupy.

1. Introduction

Nitrogen (N) is often the most limiting nutrient in agricultural systems. This makes it a top priority in any nutrient management practice. Due to its growth-limiting nature, producers are more likely to over-apply N to maximize crop yields. The overapplication of N fertilizers has led to nitrate leaching into groundwater and gaseous losses making it an ongoing issue in the state of California (California Water Boards, 2021). Recent legislation is requiring agricultural producers to report their N budget to the state and in response to this, the agricultural industry and academia have been attempting to develop N mineralization (N_{min}) models that can assist producers to account for their applied N. Due to the high degree of variability in N_{min} observed in previous studies, regional N_{min} predictor variables have been suggested as the best approach to successfully model N_{min} (Miller et al. 2018; Wade et al. 2016). Predicting N_{min} remains a challenge for soil scientists, and the determination of regional predictor variables, has remained an important area of agricultural research.

For decades now, there has been extensive research revolving around investigating accurate N_{min} predictor variables, with many potential candidates in the chemical, physical, and biological realm (Bonanomi et al. 2019; Colman & Schimel 2013; De Neve & Hofman 1996;

Kader et al. 2010; Martínez, Galatini, & Duval, 2018; Miller et al. 2018; Wade et al. 2016). There remain many challenges to developing N_{min} models. These challenges include soil heterogeneity and the role that temperature and moisture play in determining the dynamic nature of N cycling in any given regional soil profile. To date, there has yet to be any conclusive and easily measurable indices that successfully and accurately predict potential N_{min} in soils of the Central Valley of California (Miller et al. 2018). Thus, it remains a challenge for producers to effectively comply with legislative requirements, and to reduce their fertilizer inputs and costs.

2. Current State of the Literature

This review will move from macro to micro scale, from a general overview to N cycling in the environment, discussing environmental and climatic factors that affect N mineralization, down to microscopic biological and ultimately mineralogical indices studied regarding N mineralization. Along the way, this literature review will discuss how those various factors interact with each other, and which of those have been incorporated into previous models and the strength those variables had on the predictive abilities of those models. The cost effectiveness of any analysis is going to be of the utmost importance to any producer and will ultimately affect its success as an effect predictor. The variables that are ultimately included in any successful model will need to take not only cost into account, but also the ease of analysis.

Nitrogen Cycling in the Environment

Nitrogen is vital to life. Nitrogenous bases are what hold the rungs of DNA together via hydrogen bonding, forming the structure of a double helix that all life forms share. The N contained in amino acids is what make up proteins. The atmosphere on earth is composed of 78% N_2 gas (Havlin et al. 2016). Though, despite N being an omnipresent element, its plant available forms (ammonium (NH_4^+-N) and nitrate (NO_3^--N)) are rather limited in the natural world, with soil N (only a portion of which is plant available) only comprising 0.0038% of total N on Earth (Havlin et al. 2016). Before the Haber-Bosch process was discovered in the early twentieth century, N was converted to plant available forms primarily by microbial activity, and abiotic N cycling which also includes N fixation via lightning strikes (Doane 2017; Havlin et al. 2016). The conversion of N_2 gas to plant available forms of N is energy intensive and requires a complex multi-step process in both the biotic and abiotic processes. Approximately 50% of biological N fixation occurs due to the symbiotic relationship between various bacterial *Rhizobia* species and the root systems of leguminous plants (Havlin 2016). Biological N fixation converts N_2 gas into ammonium (NH_4^+) using large amounts of energy in conjunction with nitrogenase (an enzyme produced by *Rhizobia*) to split the N_2 triple bond. While the majority of the ammonium is used to form organic N compounds such as proteins, and amino acids within the plant, some is released into the soil to be converted to nitrate via nitrification and mineralized into the terrestrial system where it can be used as building blocks for flora and fauna. As those same flora and fauna die off and decompose, their proteins are depolymerized into amino acids and deaminated to available forms which are recycled through the ecosystem, resulting in various organic N-containing compounds that are consumed by microbes that enzymatically depolymerize (via proteases and peptidases) and further breaks them down into their available

parts such as amines and urea (Havlin et al. 2016). A portion of those organic compounds are stored in the form of soil organic matter (SOM) to be utilized at a future point as this pool turns over through decomposition. The N content in soils increases as SOM content increases, with total soil N being 95% composed of organic N (mostly as proteins, complex N compounds, amino acids, and amino sugars), with the remainder in inorganic forms (NH_4^+, NO_3^-, nitrite (NO_2^-), nitrous oxide (N_2O), nitric oxide (NO), nitrogen dioxide (NO_2), and elemental N (N_2)) (Havlin et al. 2016). The plant available forms are NH_4^+ and NO_3^-, which are the products of mineralization and subsequent nitrification. The majority of mineralizable N is derived from amino acids and NH_4^+-bound organic material (Havlin et al. 2016). Soil organic matter alone can provide anywhere from 25-50% of N requirements for any given vegetable crop (De Neve 2017). As the SOM is processed by microbes, any nutrients present in concentrations that exceed the biological needs of soil organisms are released back into the soil solution in their respective mineral forms to become biologically available (De Neve 2017).

The interactions between SOM, soil particles, and the soil solution are complex. Soil mineralogy can protect SOM from further decomposition and degradation from microbial or abiotic processes via "zonal organo-mineral associations" as described by Kleber, Sollins, and Sutton (2007). These zonal structures are found at the mineral surface of soil particles where SOM has connected and arranged into layers with varying degrees of attachment (Kleber, Sollins, & Sutton 2007). The layers closest to the mineral interface are more tightly held than those on the outer layers. Furthermore, the amphiphilic nature of some of these organic compounds cause micelles to form (Kleber, Sollins, & Sutton 2007). Micelles are organo-chemical aggregates that physically shield SOM in aqueous solution (Kleber, Sollins, & Sutton

2007). This zonal structure also helps to explain differences observed between the long-term stable pool of N, as well as the faster more accessible pool of N (Kleber, Sollins, & Sutton 2007).

Currently, the N cycle is composed of a plethora of recognized transformations and fates including: **ammonification** (the reduction of nitrite or dinitrogen to NH_4^+,), **mineralization** (the conversion of organic forms of N to NH_4^+, including aminization, the conversion of proteins to their amino acid forms, followed by ammonification), **nitrification** (the oxidation of ammonia (NH_3) to nitrite (NO_2^-), which is further oxidized to NO_3^-), **fixation** (N that is bound up in clay minerals and rendered biologically unavailable), **volatilization** (NH_4^+ that is converted to NH_3 and returned to the atmosphere), the reduction of NO_3^- to NO_2^-, denitrification (also known as "**nitrogen-oxide gasification**"), **immobilization** (consumption of N by heterotrophic bacteria as an energy source to break down high C:N ratio SOM), and **anammox** also known as coupled "nitrification-denitrification" (Figure 2.1) (Havlin et al. 2016; Stein & Klotz, 2016). In the current study, the transformations that will be focused on are mineralization and immobilization, with the result of the two combined processes defined as net N_{min}. We focus on mineralization of N because it represents the active conversion of organic soil N into plant available forms and is thus critical for agricultural cropping systems. While all of these processes are given proper names and appear to be separate, they all are occurring in soils simultaneously in a continuum of outcomes that resulting in net N_{min} (De Neve 2017).

The majority of the aforementioned transformations occur through enzyme-facilitated biological processes carried out by heterotrophic bacteria and fungi, but a significant amount of N transformation reactions also occurs abiotically (De Neve 2017). Doane (2017) noted that there are actually more direct transformations of N possible via abiotic processes than through biological pathways. To paraphrase Doane (2017), as abiotic pathways of N cycling receive very

little attention in the scientific world, photochemical and thermochemical processes may hold more answers than we are aware of in terms of unlocking the intricacies of terrestrial N cycling and may resolve any discrepancies between biological activity and observed measurements. This becomes particularly important when considering that for every biological N transformation, there is an abiotic equivalent. For example, Doane (2017) mentions evidence that the photochemical fixation of N_2 to NH_3 or NO_3^- occurs at the same rate as lightening fixation (approximately 2-20 Tg N $year^{-1}$). Furthermore, when considering situations where rates of biological N fixation may be low, such as excessively dry or cold systems, photochemical fixation becomes increasingly important. This has crucial implications for agroecosystems like the Central Valley, which is experiencing increasing drought conditions each year.

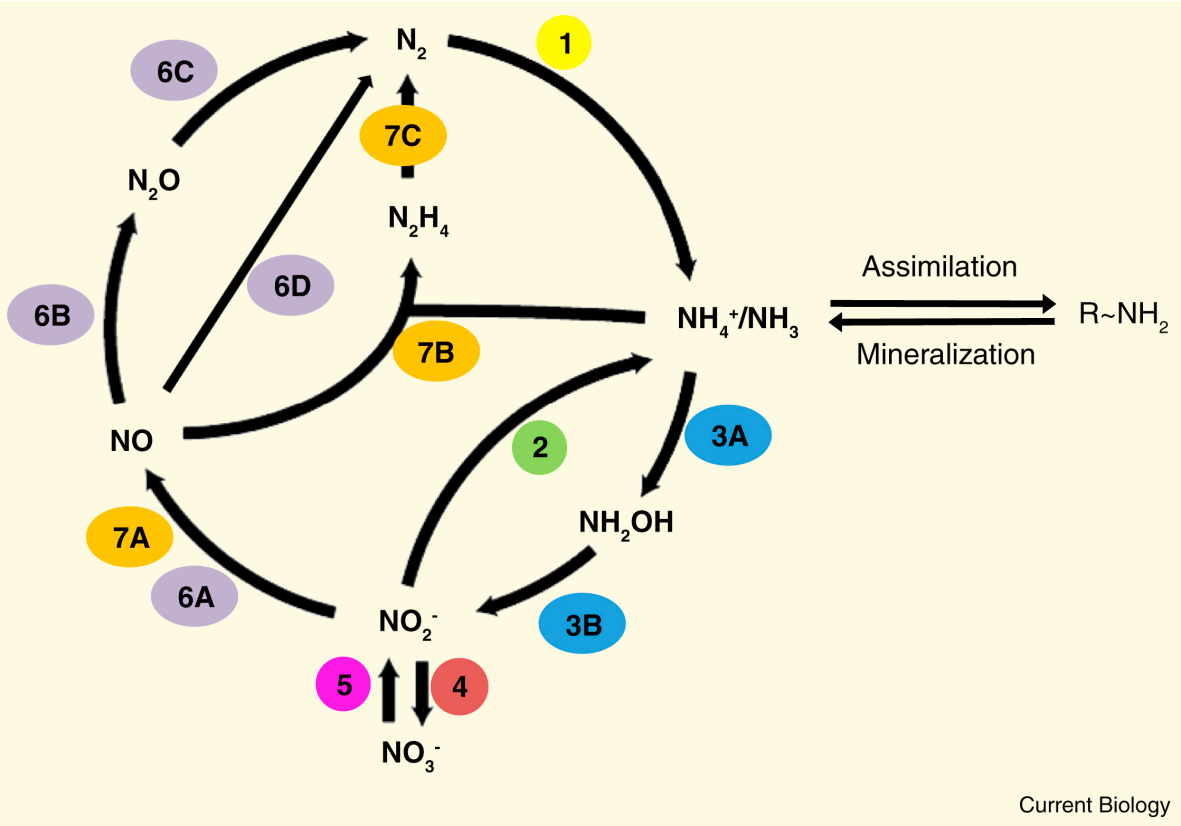


Figure 2.1: Major processes of the nitrogen cycle.

Reactions that comprise the seven major processes of the nitrogen cycle are represented by the numbered circles. Ammonification may be accomplished either by process 1, reduction of dinitrogen (also referred to as 'nitrogen fixation' or 'Nif'), or by process 2, dissimilatory nitrite reduction to ammonium (DNRA). Nitrification is composed of process 3, oxidation of ammonia to nitrite (also referred to as 'nitritation'), and process 4, oxidation of nitrite to nitrate (also referred to as 'nitratation'). Process 5, reduction of nitrate to nitrite, can be coupled to processes 2, 6 or 7 in a population or a community. Denitrification is shown as process 6, which is also referred to as 'nitrogen-oxide gasification'. Anammox is shown as process 7 and is also referred to as coupled 'nitrification–denitrification'. (Stein & Klotz 2016)

Factors that Drive Nitrogen Mineralization: Environment and Climate

There are many environmental factors that affect N_{min}. Large scale factors include soil moisture content as controlled by precipitation and irrigation; soil temperature which fluctuates on a climatic, seasonal, and regional scale; soil pH which controls nutrient availability for microbes which carry out most N cycling processes; and soil aeration, which is also critical as many microbes are aerobic and waterlogged or compacted conditions can lead to N volatilization and leaching (De Neve 2017; De Neve & Hofman 2002; Stein & Klotz 2016).

There are ideal conditions in terms of temperature and moisture for any microbial process (i.e. nutrient cycling). For N mineralization, the ideal conditions for laboratory incubations studying optimal N cycling are between 20-30 °C and approximately 20-30% soil moisture content, or field capacity, as these ranges represent average optimal field conditions (Cassman & Munns, 1980). At lower temperatures and moisture content, nutrient cycling slows significantly (Cassman & Munns, 1980). While at higher temperatures and moisture content, N cycling varies more widely. For example, the optimum N mineralization temperature is between 37-50°C, but optimum nitrification takes place at a lower temperature range of 15-25°C (Antoniou et al. 1990; De Neve, Hartmann, & Hofman 2003).

The effect of temperature and moisture on nutrient cycling partially explains the differences seen between mineralization rates in a humid tropical soil versus an arid Mediterranean soil (Martínez et al. 2018). With increased temperature and moisture in a humid tropical environment, the rate of nutrient cycling is increased when compared to an arid-Mediterranean environment (Dirks et al. 2010; Khalil, Hossain, & Schmidhalter, 2005; Martínez et al. 2018; Myers, Weier, & Campbell, 1982). In an arid-Mediterranean environment, the lack of precipitation can limit or slow nutrient cycling as many microbial processes are highly dependent

on moisture content (Dirks et al. 2010). The strong effect of temperature and moisture further demonstrates the importance of regional modeling, which are much more accurate than a broad over-generalized model. These two variables highly control the rates of microbial processes, and, thus, should always be considered as an overarching contributor when building any model.

Various soil properties control the microbial responses to changes in temperature and moisture. One example of a soil property that would control microbial responses to variations in temperature and moisture content would be a change in SOM present in soils, as SOM can have an insulative effect while also adding porosity to soil (Khaleel, Reddy, & Overcash 1981). Practices such as cover cropping or residue incorporation alter the amount of SOM in soil.

Further examples of soil properties that alter soil sensitivity to changes in temperature and moisture are soil texture and structure (Cassman & Munns 1980; De Neve 2017; Xiao et al. 2019). Soil texture and structure are closely related to each other, with texture considered the fixed proportion of sand, silt, and clay, and soil structure is considered subject to alteration from management (i.e. tillage and compaction) and weathering (Hassink 1992). Texture plays a major role in soil's ability to influence structure, such as aggregation which impacts water holding capacity through changes in the soil's bulk density and pore size distribution. For example, increased sand content results in greater proportions of larger pores, and, thus, soils will dry out and heat up more quickly in a sandier soil compared to a siltier or clay soil (De Neve 2017). Structure plays a similar role by driving porosity, aeration, and water infiltration via the specific arrangement of soil particles in the profile which is highly influenced by disturbance (Hassink 1992). Increasing the SOM content can help insulate the soil, altering its structure, as well as increase its water holding capacity; and thus, management can alter a soil's temperature and moisture sensitivity (De Neve 2017, Hassink 1992).

Organic matter is the soils main source of both carbon (C) and N. Carbon is inextricably linked in its relationship to N and the two are required in the majority of basic components required for life. In N cycling research, this has been described as the "C Connection" by Hart et al. (1994). The "C Connection" theory states that N cycling is controlled by the availability of C, and that as easily accessible C declines, so does the consumption of N by N cycling microbes (Hart et al. 1994). The "C Connection" theory is further supported by Martínez et al. (2018), whose most successful model of N mineralization prediction also included a measure of soil carbohydrate content.

Cropping System and Residue Addition Effects on N Mineralization

Organic matter additions to soils can be made via cover cropping, as discussed above, crop residue incorporation, or applications of manure, compost, biosolids, and food wastes. Residue incorporation is important for returning C and nutrients to the soil that were removed with the previous crop. As cover cropping and residue incorporation become more common in agriculture due to their influence on soil health parameters (increased water holding capacity, SOM and nutrient additions, erosion control, etc.), they have been implicated as important drivers of nutrient cycling (Cabrera, Kissel, & Vigil, 2005; Chen et al. 2014; De Neve, & Hofman, 2002; Kassink 1992; Khaleel, Reddy, & Overcash, 1981; Kaur, Cihacek, & Chatterjee, 2018; Redin et al. 2014; Rodríguez-Lizana et al. 2010; Walela et al. 2014). Organic matter is considered to be the main contributor of mineralizable N in soils. Thus, both the incorporation of crop residues and cover cropping cause fluctuations in the SOM pools, as they are the main source of new SOM in many agricultural systems (Shennan, 1992).

Historically, the C:N ratio has been considered the main contributor of how N-cycling microbes respond to N additions in terms of whether it meets their N requirements. This results in either immobilization or mineralization of N. The justification for this connection between C:N ratio and N_{min} is due to the stoichiometric relationship between the C and N metabolic requirements of saprophytic microbes and the C and N supplied by the SOM (Bonanomi 2019). Though, recent work has shown that not only is the C:N ratio important in determining microbe's response to residue additions, but also the soil's properties and the composition of those residues (Cabrera et al. 2005; Chen et al. 2014).

De Neve (2017) discussed various fractionation methods that have been used in conjunction with the C:N ratio in an attempt to characterize residues that are added to soils in an effort to predict N release from those residues. The main issue with these fractionation methods is that they give different results depending on the method used, so they are not easily comparable. A review by Chen et al. (2014) collated several useful indices to better predict how specific types of residue additions will decompose in soil upon incorporation. The plant residue quality modified index (PRQMI) as described by Tian et al. (1995) and modified by Kumar and Goh (2003) uses the C:N ratio, lignin and polyphenol concentrations in relation to changes in soil inorganic N for the purpose of predicting N release from residue additions. Chen et al. (2014) also discussed the organic matter quality index (OMQI) (as described by Khalil et al. 2005), to allow both plant and animal residue qualities to be assessed in predicting N mineralization using the parameters of pH, the residue C:N ratio, plus the soil cation exchange capacity. The OMQI was 67% effective at predicting aerobic decomposition rates of residues and used to help predict N mineralization and nitrification under different soil types (Chen et al. 2014). Both PRQMI and OMQI take into account how the different components of residues degrade at varying rates and

to different degrees, allowing for a more accurate representation of how residues will contribute to N mineralization than by just utilizing the C:N ratio alone (Chen et al. 2014).

While climate, management and residues influence large-scale N mineralization rates over the landscape and especially within a region, now it is time to transition into the microscopic realm of soils. Here, within the soil microcosm, previous research shows how the large and fine-scale factors influence each other to orchestrate N cycling. Within this fine-scale domain, there are three categories that will be discussed: the chemical, mineral, and biological factors that play an important role in N mineralization.

Modelling and Predicting N Mineralization: *Chemical, Mineralogical and Biological Indicators*

Attempts at modelling, predicting and estimating N mineralization from native SOM has been an ongoing effort in the scientific community for several decades (Bonanomi et al. 2019; Cabrera & Kissel, 1988; Cassman & Munns, 1980; Colman & Schimel, 2013; Curtin et al. 2017; De Neve & Hofman 1996; Geisseler & Miller, 2019; Griffin et al. 2007; Jilling et al. 2018; Kader et al. 2010; Kaur, Cihacek, & Chatterjee, 2018; Martínez, Galatini, & Duval, 2018; Miller et al. 2018; Myers, Weier, & Campbell 1982; Ros, Temminghof, & Hoffland, 2011; Schomberg et al. 2009; Sharifi et al. 2007; Wade et al. 2018; Zhu et al. 2014). Predicting N mineralization in agricultural soils is critical to the management of both crop requirements and mitigating NO_3^- leaching into groundwater and aquifers. Across the agroecological science community, scientists have struggled to determine a robust and accurate indicator of potentially available N, also known as mineral N or the sum of NH_4^+-N and NO_3^--N (Cassman & Munns 1980; Colman & Schimel 2013; Curtin et al. 2017).

There are numerous biological and chemical soil indices that show promise in terms of being able to predict N_{min}, including total C and N, various N extractions (including, but not limited to: hot water KCl, $NaHCO_3^-$, dissolved organic N, and water extractable organic N), different iron fractions that sorb strongly with N, and pH (Curtin et al. 2017; Jilling et al. 2018; Martínez, Galatini, & Duval, 2018; Miller et al. 2018; Sharifi et al. 2007; Schomberg et al. 2009; Wade, Horwath, & Burger 2016; Wade et al. 2018). Soil organic matter fractions have also been studied extensively to determine the main driver of potentially available N. De Neve (2017) recommends as a general rule to estimate rough N_{min} rates (in lieu of actual measurements), applying a 2-3% N_{min} rate under temperate maritime climates; but they admit this is a gross over-simplification that varies greatly with soil texture and should be used with great prudence. All of this ongoing research revolving around potential N_{min} predictors has been undertaken in an effort to find an easily measurable, rapid, and affordable soil test that could be incorporated into any fertilizer program with relative ease within any local soil testing lab (Curtin et al. 2017).

A commonality across studies is that predicting available N is more complex than any limited information a single predictor variable could provide; and any successful prediction will require multiple factors to be taken into account. Currently, there are very few tools available to accurately predict N_{min} and are limited at a regional scale. Environmental factors, like climate, soil temperature and moisture, management regime, residue quality and management, and the previous year's crop all play an important role in predicting the next growing season's mineralizable N (Sharifi et al. 2007; Tian, Brussard, & Kang 1995; Wade, Horwath, & Burger 2016). Many studies have concluded that likely there will never be an all-encompassing model that can be universally applied and that regional models will need to be developed individually based on various soil properties, SOM composition, climate, and management (Wade et al.

2016). Thus, until there is a breakthrough in soil science that allows for the development of a single-variable N prediction tool, the regional multivariate modeling approach is the next best step (Miller et al. 2018; Wade et al. 2016). In the following sections, a further in-depth discussion of these various chemical, mineralogical, and biological indices will give us a clear idea of where the literature currently stands in terms of predicting and modeling N_{min}.

Chemical Indicators

If one single chemical index has been implicated the most in predicting N_{min} in the literature, it would be total N. As mentioned previously, total N, as measured by combustion analysis, has classically been considered one of the strongest indicators of potential N_{min} (Martínez, Galatini, & Duval, 2018; Wade, Horwath, & Burger 2016). However, recent research has shown that total N is not always the strongest or best predictor (Geisseler & Miller 2019; Miller et al. 2018). The lack of predictive ability by total N is demonstrated in a study by Wade, Horwath, and Burger (2016), who found that while total N had the strongest correlation with N_{min} across all sites, it was weak. Wade, Horwath, and Burger (2016) also found that between cover-cropped (CC) and non-cover-cropped (NCC) treatments there were no strong indicators or predictors. What has been observed in other studies is that total N, when used in conjunction with other indicators, strengthens overall predictions of N_{min}, but is not the best single indicator on its own as it was once considered (Wade, Horwath, & Burger 2016).

Sharifi et al. (2007) found that along with total N, another chemical indicator that is a proxy for hydrolyzed organic N (i.e., depolymerized amino acids, proteins, nucleotides, etc.), as measured via UV absorbance of $NaHCO_3$ soil extracts at 260 nm (UVN) (r^2=0.71), had a strong correlation with potential N_{min} (r^2=0.67). The authors suggested this relatively reliable and

simple analysis be considered as a general soil test as an indicator of potential N_{min}. UVN was also found to strengthen potential N_{min} predictions in two other studies, one by Martínez et al. (2018) and the other by Curtin et al. (2017).

De Neve (2017) states that pH undoubtedly has an effect on N_{min}. With decreased N_{min} rates resulting from lower soil pH. De Neve (2017) speculates that this is likely due to decreased microbial activity at lower pH values.

Mineralogical Indicators

The strongest predictive potential N_{min} models for both high and low OM soils in a study by Miller et al. (2018) utilized several variable types. First, a measure of soil texture and mineralogy, as well as a measure of SOM quantity and quality. The strongest mineralogical component they found was pyrophosphate extractable iron (Miller et al. 2018). Wade et al. (2018) supported the Miller et al. (2018) finding by showing through structural equation modeling that when total N, and pH mediated sorption of N to poorly crystalline iron-oxides were included, it helped to best describe N_{min}. A rationale for this interaction is provided by a Jilling et al. (2018) study, which hypothesized that mineral-associated-organic-matter was a significant mediator of available N in soil solution. This is due to N-compounds sorbing strongly to mineral surfaces and competing with microbes (Jilling et al. 2018). This supports the general soil chemistry sorption phenomenon, which shows that compounds with high ionic strength will sorb strongly to mineral surfaces. Furthermore, these strong sorption interactions will compete with each other and thus these compounds also compete with microbes for edge sites. Iron oxides bind to organic N-containing compounds very strongly and thus mediate N-turnover by microbes (Jilling et al. 2018).

The quantity and rate of N mineralized from SOM is determined in large part by soil texture (De Neve 2017). This is rather intuitive as texture determines water holding capacity, as well as bulk density, soil aeration, water infiltration, the interactions between SOM and clay content, and the flow of soil solution. All of these properties strongly influence microbial processes. A textural component (i.e. sand, silt or clay content) was found to be an important predictor variable in many studies (Cabrera et al. 2005; Colman & Schimel, 2013; Martínez et al. 2018; Miller et al. 2018; Wade et al. 2018). Texture's effects on soil porosity and overall pore size distribution directly influences decomposition and N mineralization through mediating the flow of water and air in the soil. This fluctuation of water and air is necessary for microbial communities to biologically mineralize N. Hassink et al. (1993) found that decomposition rates were higher (and thus a corresponding increase in the proportion of mineralized organic N) in sandier soils when compared with siltier and clay soil, due to physical protection afforded in smaller pore size distributions. The mechanism by which small pores protect SOM is via clay layers enclosing and trapping the organic particles, making them inaccessible to microbes (Hassink 1992). Disruption of these protected aggregates (i.e. sieving) results in an increase of N_{min} (Hassink 1992). Cabrera et al. (2005) supports this further, stating that when comparing nine different soils, the best predictor for potential N_{min} was the ratio of sand content to water content at field capacity. De Neve (2017) also mentions the importance of physical protection of SOM and that heavier clay-rich soils reduce N_{min} rates.

Biological Indicators

There have been mixed reported results on the various potential biological indices for predicting potential N_{min} (Kader et al. 2010, Miller et al. 2018). As N cycling is largely a biological process, the degree to which any analyses can predict its potential mineralization is complicated by the fact that biological processes are highly dependent on all the previously discussed properties and variables. This area of research has proven to be one of the more convoluted fields of study and has by far the highest degree of contradicting information found in this area of research. There are very few biological analyses that have resulted in any overarching consensus among researchers, they are however becoming increasingly important in their ability to assess soil health and will likely become more widely available as the methods become more consistent and predictable. Thus, the following review will tread lightly upon this topic. As most biological assays are not typically found in soil testing labs, they will not be more thoroughly investigated in the current study. However, biological indicators are discussed in this review as they are still relevant in developing an understanding of the current state of the literature. Therefore, the two biological trends that are most relevant are focused on general enzymatic analyses as well as soil respiration measurements and their connections to potential N_{min}.

The depolymerization of N is often considered the rate-limiting step in N_{min} (Jilling et al. 2018; Wade et al. 2018). As depolymerization of N is a microbially mediated process, various enzymatic analyses have been shown to be strongly correlated with potential N_{min} (Jilling et al. 2018; Miller et al. 2018). In low SOM soils, Miller et al. (2018) found that fluorescein diacetate (FDA) hydrolysis (a general enzyme assay), pyrophosphate extractable iron, and silt content were the main variables contributing to potential N_{min}. These findings could be due to the connection between increased enzymatic activity resulting from sorption of SOM to mineral

surfaces as described by Jilling et al (2018). The authors theorized that the process of increased enzymatic activity near sorption sites is because of the protection provided from fluctuating pH, temperature, and ionic strength that mineral surfaces provide.

Soil respiration has been found in several studies to be a good indicator for potential N_{min}, more specifically the CO_2 burst upon rewetting of soils (CO_2 burst). Soil respiration as an indicator of potential N_{min} was mentioned by Wade, Horwath, and Burger (2016), who found that the CO_2 burst was a consistent and reliable (although weak) proxy for potential N_{min}. Soil respiration as an indicator of potential N_{min} is also supported by a study from Schomberg et al. (2009) who found that CO_2 burst and total N were good predictors of potential N_{min}. Soil respiration as an indicator of potential N_{min} was further supported by Curtin et al. (2017), who also found that the CO_2 burst values were good indicators for predicting potential N_{min}. Respiration is one of the simplest measurements of microbial activity, and thus logical that numerous studies have found it to be strongly correlated with potential N_{min}. Soil respiration and enzyme production have been shown to be robust general indicators of overall microbial activity.

Summary of Nitrogen Mineralization Modeling

Recent research has led to the development of numerous N_{min} prediction models. However, here we focus on modelling efforts that were developed from the same or similar climates as our study (i.e. Mediterranean or semi-arid).

A study by Miller et al. (2018) investigated N_{min} using 10-week undisturbed core incubations of California soils with low SOM content (in the same range with our study) and developed the following N_{min} prediction model after using multiple linear regression analysis:

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

$R^2 = 0.604$

Wherein the model parameters are defined by the following abbreviations: TC = total C (%), silt = proportion of silt, and FDA = fluorescein diacetate hydrolysis (mg FDA kg^{-1} oven-dry soil hr^{-1}).

Another recent study by Wade, Horwath, & Burger 2016 found after using partial least squares regression analysis for modeling N_{min} in California soils, the factors that best explained N_{min} at 105 days of incubation in their non-cover cropped treatments across all fields were initial inorganic N content (the sum of ammonium-N and nitrate-N), dissolved organic C, and total C:N ratio, resulting in an adjusted-R^2 of 0.18 across all studied regions.

Clivot et al. (2017) found in their simulated N_{min} prediction study using multiple linear regression that across 65 fallow field sites in France (nine out of the 65 were classified as Mediterranean), soil organic N content, clay content, pH, and the C:N ratio of SOM described 56% of the variation in potential N_{min}.

Coleman and Schimel (2013) found in their continental N_{min} predictive modeling study using a combination of linear regression and structural equation modeling (84 soils covering North America, Puerto Rico, and Hawai'i) that 33% of the variance was explained by mean annual precipitation, soil C and N content, and clay content.

Osterholz et al. (2017) found in their N_{min} predictive modeling study investigating conventionally managed soils of both Israel and the United States, that after performing multiple linear regression analysis there were six SOM size fraction predictor variables: particulate organic N, non-particulate organic matter associated N, total N of the cold-water extractable SOM, total C and N of the hot-water extractable SOM, as well as NH_4^+ content of that fraction. This model resulted in an R^2 of 0.80.

In summary, predicting N_{min} is complex and controlled by several factors which vary in areas with different soils and climates. Commonalities across studies include textural and SOM related properties. These results reinforce the importance of generating a regional model is critical as it will hopefully narrow down the possible predictors to a select few. As it is unlikely that researchers will ever determine a single predictor variable, Ros, Temminghoff, and Hoffland (2011) have recommended that researchers release expectations of this ideal and embrace the multi-factor approach that is clearly required. Our research will be focused on the Central Valley of California, which is a Mediterranean climate, thus our findings will also be applicable to other semi-arid environments.

Objectives

The objectives of this study include (1) monitoring and quantifying potential N_{min} over the growing season (approximately March through October) and evaluate the importance of soil and environmental variables across the Northern Central Valley of California in an effort to (2) improve upon existing models that can be used by producers to determine available N for their fertilizer budgets; and to (3) further study regional N_{min} variability by accounting for the effect of residue additions on potential N_{min} through field trials and laboratory incubations to improve the model's N_{min} predictability.

This study has several phases. An incubation study, which spanned over two growing seasons from 2019 through 2020, consisting of incubations of undisturbed soil cores and their disturbed counterparts to determine the N_{min} potential of each site. The soils utilized were collected from seventeen annual cropping sites throughout the northern portion of California's Central Valley, spanning a large range of soil types. Undisturbed soil cores were incubated to

determine potential N_{min}, and the soils were also fully characterized to develop a best fit model of undisturbed core N_{min}. To support the larger project, two additional studies were done which consisted of a field trial involving seven common crop residues (*Zea mays* (corn), *Citrullus lanatas* (watermelon), *Carthamus tinctorius* (safflower), *Helianthus annuus* (sunflower), *Sorghum bicolor* (sorghum), *Solanum lycopersicum* (processing tomatoes), and *Gossypium hirsutum* (cotton)), as well as two laboratory incubations using processing tomato residues and *Brassica oleracea var. botrytis* (broccoli) residues.

The field trial and residue incubations were performed in an attempt to understand how residue type and quality under field and laboratory conditions play a role in nitrogen management. This study will provide useful data and insight for growers and researchers to improve upon best management practices and build our understanding of N turnover in semi-arid Mediterranean regions.

3. A Nitrogen Mineralization Study in the Central Valley of California

3.1 Introduction

California is highly diverse in its agricultural production and specialty crops, producing over 400 different agricultural goods, more than 60% of the nation's fruits and nuts, and over 30% of the nation's vegetables (California Department of Food and Agriculture (CDFA), 2021). The Central Valley in particular provides most of the state's fruit and nut orchards, grapes, cotton, processing tomatoes, rice, corn, and more (CDFA 2021). Nitrogen (N) fertilizer management has been gaining recognition as a vital area of research, especially after the passage of the Sustainable Groundwater Management Act (SGMA) in 2014. SGMA was passed in response to the Irrigated Lands Regulatory Program (ILRP) in 2003 (California Water Boards, 2021). SGMA and ILRP in conjunction with the Salt and Nitrate Control Program requires producers to report their N fertilizer use with the goal of minimizing nitrate loading into groundwater (California Dept. of Water Resources, 2021; California Water Boards, 2021; Central Valley Salinity Coalition, 2021). In an ongoing effort to assist growers in reducing their fertilizer applications and improve water quality across the state, one research focus has been on quantifying N mineralized from native soil organic matter (SOM) (Miller et al. 2018; Wade, Horwath, & Burger, 2016). Differences in climate, biology, and soil type all contribute to the large variability observed in N_{min} patterns across and within regions. Thus, regional modeling has been suggested as the most successful approach to predicting N mineralization (N_{min}) (Miller et al. 2018; Wade, Horwath, & Burger, 2016).

The biological processes responsible for N cycling and mineralization in soil are highly dependent on large-scale environmental factors such as climate, parent material and topography. The microbial mechanisms that are involved in N cycling are highly sensitive to temperature and

moisture, thus the soil properties directly linking those environmental conditions with the microbial communities being subjected to them (i.e. texture and SOM content) are likely to be included in any N_{min} prediction model. Soil texture and structure affects porosity and water holding capacity (WHC), as well as soil surface area which directly influences the accumulation and protection of SOM (De Neve 2017; Havlin et al. 2016). Organic matter provides a large portion of nutrients to the biota present, as well as increased surface area, and enhanced WHC (Havlin et al. 2016).

Soil organic matter is the main pool of organic N in terrestrial ecosystems. Havlin et al. (2016) estimates that SOM contains approximately 5% N, and that each year about 1-3% of soil organic N is converted into an inorganic and plant available form. While SOM content varies widely across soil types, soils in the Central Valley have low SOM contents of generally less than 3%. Previous studies have found various SOM fractions and SOM quality to be significantly correlated with N_{min}, some examples include total N, particulate organic matter (POM), and permanganate oxidizable carbon (POXC) (Bu et al. 2017; Miller et al. 2018; Wade, Horwath, & Burger, 2016). One of the main contributors of SOM in Central Valley soils in conventionally managed cropping systems is the previous crops residue (Miller et al. 2018; Wade, Horwath, & Burger, 2016). Previous studies have recommended further investigation into the contribution of these residues to N_{min} (Miller et al. 2018; Wade, Horwath, & Burger, 2016).

An area of research that has received little attention is the effect of a fully developed root system on seasonal site-specific N_{min} (Cheng et al. 2014; Fornara, Tilman, & Hobbie, 2008; Zhu et al. 2014). Roots and specifically their exudates have been found to have a considerable effect on N cycling in the rhizosphere (Cheng et al. 2014; Zhu et al. 2014). This is likely due to the composition of the exudates and the effect they have on the surrounding microbial community

(Fornara, Tilman, & Hobbie 2008). As this study focuses on seasonal N_{min} trends, we decided to further investigate the potential effects that a fully developed root system may have.

This project is focused on developing an understanding of N_{min} dynamics in agricultural soils located in the Central Valley of California. Previous research has resulted in accurate models for high SOM regions of the Central Valley. However, the same study suggested further study of N_{min} in regions with low SOM content, to determine which soil properties best describe the variability observed (Miller et al. 2018). There are several goals for this study, namely to assess and compare the high degree of variability in N_{min} observed within our own N_{min} datasets and reported in other studies; to test whether the previous season's crop or biological factors such as the presence of fully developed root systems significantly affected N_{min}; as well as determining the soil properties in the Central Valley that most effectively describe the variability observed for N_{min} in undisturbed soil cores and in disturbed (sieved) soil samples with an emphasis on soils with low SOM content. Potential properties were selected based on common analytical methods that would be found in soil testing labs. The results shall contribute to an online web tool that can be used by producers for estimating N availability by entering the data obtained from their soil test results.

Hypotheses

Based on the importance of soil texture as the matrix in which microbes interact with their source of N, and SOM as their N source, we hypothesized that (1) the best fit model for the pre-plant undisturbed core N_{min} data would include a textural component, as well as a SOM related component.

Due to the high level of variability observed in other studies' N_{min} trends, we developed several hypotheses to potentially explain the anticipated N_{min} irregularities in our own datasets. We hypothesized that (2) variations in handling techniques would result in significantly different N_{min} trends between the undisturbed core and disturbed soil samples, and that (3) the field moist (FM) treatments would mineralize significantly less N than the 60% WHC treatments.

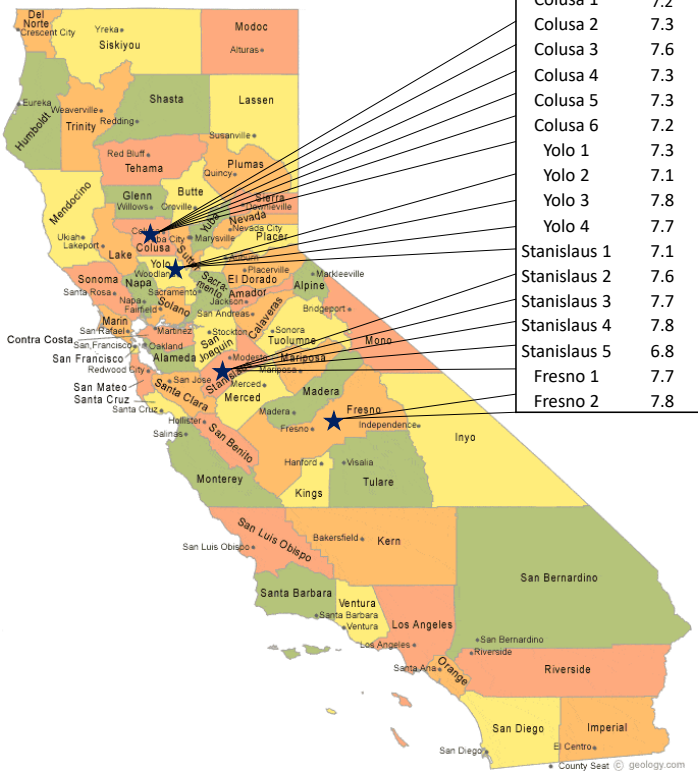
Earlier studies have also suggested that the previous season's crop may affect the next season's N availability, so we investigated whether the pre-plant undisturbed core N_{min} would be potentially affected by the previous seasons crop. We also hypothesized that (4) there would be significant differences in the disturbed N_{min} at 60% WHC between sites due to the presence of established plant roots.

Finally, we compared our undisturbed soil core model with a recent independent study by Miller et al. (2018) that also developed an undisturbed soil core model from the same region, and we hypothesized that (5) this research would lead to an improved N_{min} prediction model for low SOM soils in the Central Valley.

3.2 Materials and Methods

In this study, potential N_{min} and its regional variability were determined by collecting soil samples across California's Central Valley prior to and throughout the growing season and incubating them at a constant temperature either at field moisture or an optimal moisture content. Soils were collected from a total of seventeen sites (eleven sites in 2019, and six sites in 2020) across the Central Valley of California (Figure 3.1). The northernmost site was located in Colusa County (39.2, -121.9) and the southernmost site was in Fresno County (36.3, -120.1). The Central Valley is composed of both the Sacramento Valley in the north, and the San Joaquin

Valley in the south. The soils were mainly formed from alluvial deposition from the surrounding mountain ranges of the Sierra Nevada and Cascades to the east, and the Coastal Ranges to the west. None of the selected sites had a history of cover cropping or application of organic fertilizers. Crop types in the study year varied among sites and included corn (*Zea mays*), watermelon (*Citrullus lanatas*), safflower (*Carthamus tinctorius*), sunflower (*Helianthus annuus*), sorghum (*Sorghum bicolor*), processing tomatoes (*Solanum lycopersicum*), and cotton (*Gossypium hirsutum*). Each site's in-season crop and the previous season's crop are shown in Table 3.1. Irrigation management included sub-surface drip (majority of sites), flood irrigation, and one rain-fed system. All of the selected sites were conventionally managed. Initial soil samples were collected pre-planting and prior to tillage in 2019 and 2020. The top hardened layer of soil and any plant material was first removed, then two 15-cm long undisturbed cores were taken in 4.5 mm diameter plastic sleeves in each of four replicated areas at every site. Those cores were incubated at 25 ºC for 10 weeks and analyzed for mineral N content. In addition, several samples were taken from the same layer with a soil probe from the area surrounding the core sampling locations. The samples from each core location were then combined, homogenized and stored in a cooler on ice with the undisturbed cores until returned to the lab and stored in a 4 °C cold room until processing. Through the remainder of the growing season, subsamples were taken from each site and incubated approximately every 5-6 weeks until the harvest date in the fall from the same layer with a soil probe. Upon completion of the incubation, the soils were analyzed for mineral N content. The potential N_{min} data along with the soil characterization data were statistically analyzed to determine which properties most significantly affected N_{min} in Central Valley soils.



Site	pH	EC (µS cm^{-1})	Texture	Pd (g cm^{-3})	Soil Organic Matter (%)
Colusa 1	7.2	97	Sandy loam	1.49	1.6
Colusa 2	7.3	96	Silty clay	1.21	2.9
Colusa 3	7.6	184	Silty clay	1.17	2.6
Colusa 4	7.3	173	Silt loam	1.22	1.7
Colusa 5	7.3	162	Loam	1.25	1.8
Colusa 6	7.2	219	Silty clay loam	1.21	2.9
Yolo 1	7.3	96	Clay	1.34	2.0
Yolo 2	7.1	98	Clay loam	1.53	1.7
Yolo 3	7.8	124	Clay loam	1.35	1.8
Yolo 4	7.7	87	Clay loam	1.36	1.9
Stanislaus 1	7.1	64	Sand	1.71	0.6
Stanislaus 2	7.6	261	Clay	1.42	2.1
Stanislaus 3	7.7	332	Clay loam	1.29	1.7
Stanislaus 4	7.8	293	Silty clay loam	1.33	1.9
Stanislaus 5	6.8	152	Sandy loam	1.53	1.6
Fresno 1	7.7	1454	Clay loam	1.35	1.5
Fresno 2	7.8	1029	Clay	1.32	1.8

Image credit: https://geology.com/county-map/california.shtml accessed 2/18/2020

Figure 3.1: **County map of California featuring each site's summary data:** soil pH, electrical conductivity (EC), texture, bulk density (Pd), and soil organic matter (%). Texture was determined by particle size analysis. pH and EC were measured using a 2:1 distilled water and soil solution. Soil organic matter is based on the soil total C content (Pribyl 2010). See the materials and methods section for analyses details.

Table 3.1: Location by county, soil series, previous and sampling year's crops are shown. Soil series information was provided by the Natural Resources Conservation Service Web Soil Survey (WSS, 2021).

ID	County	Soil Series	Crop in Study Year	Previous Year's Crop
C1	Colusa	Vina loam	Tomatoes	Wheat
C2	Colusa	Sacramento clay	Safflower	Wheat
C3	Colusa	Sycamore silty clay loam	Sorghum	Corn
C4	Colusa	Vina loam	Corn	Sunflower
C5	Colusa	Moonbend silt loam	Sunflower	Tomatoes
C6	Colusa	Vina loam	Corn	Sunflower
Y1	Yolo	Tehama loam	Sunflower	Corn
Y2	Yolo	Tehama loam	Corn	Malting Barley
Y3	Yolo	Yolo silt loam	Tomatoes	Tomatoes
Y4	Yolo	Yolo silt loam	Fallow	Tomatoes
S1	Stanislaus	Tujunga loamy sand	Watermelon	Sweet Potato
S2	Stanislaus	Capay clay	Tomatoes	Watermelon
S3	Stanislaus	Capay clay	Tomatoes	Tomatoes
S4	Stanislaus	Capay clay	Tomatoes	Tomatoes
S5	Stanislaus	Dinuba sandy loam	Honeydew Melon	Watermelon
F1	Fresno	Cerini clay loam	Tomatoes	Tomatoes
F2	Fresno	Calfax clay loam	Cotton	Cotton

Soil Incubations

The undisturbed cores were incubated at 60% WHC and 25 °C for 10 weeks to determine potential N_{min}. A side port syringe needle and D.I. water were used to adjust the soil moisture content in the cores at the start of the incubation. The cores were covered with a piece of perforated plastic wrap to allow for gas exchange. The samples were maintained at 60% WHC for the duration of the incubations, with weekly moisture adjustments. After 10 weeks, soils were

sieved to 4 mm and analyzed for mineral N (ammonium-N (NH_4^+-N) plus nitrate-N (NO_3^--N)) utilizing the methods described below (see Soil Analyses).

The samples collected from the field sites throughout the growing season were sieved to 4 mm and two 6-g subsamples were incubated in 50 ml centrifuge tubes. One subsample was incubated at field moisture, the other was brought to 60% WHC with a pipette and DI water. Soil moisture content was also maintained throughout the incubations by adjusting it at weekly intervals. After five weeks of incubation at 25 °C the subsamples were analyzed for mineral N. N mineralization was calculated for both the 10-week and 5-week incubations by subtracting the initial mineral N content from the final N content measured at the end of the incubations. The N_{min} at field moisture was normalized by expressing it in percent of N_{min} at 60% WHC. These values will be referred to as "relative" N_{min}.

Soil Analyses

Field-moist samples were sieved to 4 mm and analyzed for gravimetric water content, WHC, and extracted for available mineral N using methods described below. Gravimetric water content was determined by taking field-moist soil subsamples and placing them in the oven for 24 hours at 105 ºC. To determine WHC, soils were put into Q5 filter-lined funnels placed into beakers filled with deionized (DI) water and allowed to saturate. Then the soil-filled funnels were removed from the water, covered with plastic wrap to reduce evaporation, and allowed to freely drain for one hour. After draining, the soil was weighed and oven-dried at 105 °C for 24 hours, then reweighed. The water removed during oven-drying is considered 100% WHC. Bulk density was measured by calculating the volume and weight of soil in each undisturbed core, followed by measuring the gravimetric water content of subsamples collected from the

surrounding soil. This allowed us to determine the oven-dry weight of the soil within the cores. The oven-dry weight of the soil core was used along with the volume to calculate the soil bulk density.

In the spring, the first pre-plant subsample soils were analyzed within one week for microbial biomass carbon (MBC) via the chloroform extraction method followed by potassium sulfate (K_2SO_4) extraction as outlined by Horwath and Paul (1993) and analyzed via combustion on a Shimazdu TOC-VCSH. Once analyses on field-moist soil were completed, the soils were air-dried on the bench top.

For NH_4^+-N and NO_3^--N analysis, soils were extracted using methods described by Mulvaney (1996). Briefly, 6-g subsamples of fresh soil were extracted with 30 ml of 0.5 M K_2SO_4 on a reciprocal shaker for 1 hour and then strained through Q5 filter paper. Ammonium-N was analyzed using a colorimetric method described by Verdouw et al. (1978) and adjusted by Forster (1995). The colorimetric reaction was initiated with reagent A, composed of sodium nitroprusside ($C_5H_4FeN_6Na_2O_3$), sodium salicylate ($C_7H_5NaO_3$), sodium citrate ($C_6H_5Na_3O_7$), sodium tartrate ($C_4H_4Na_2O_6$) dissolved in DI water, followed by the addition of reagent B, composed of sodium hydroxide (NaOH) and bleach dissolved in DI water. After the addition of reagents A and B to the K_2SO_4 extracts, samples were reacted for between one and four hours and then analyzed on a Shimadzu UV 1820 spectrophotometer at 650 nm. Nitrate was analyzed using a method adapted by Doane and Horwath (2003) which involved a colorimetric reaction utilizing a reagent comprised of vanadium (III) chloride (VCl_3), sulfanilamide ($C_6H_8N_2O_2S$), and N-(1-naphthyl)ethylenediamine dihydrochloride ($C_{12}H_6Cl_2N_2$) dissolved in diluted hydrochloric acid (HCl). Once reagent additions were made, samples were reacted for a minimum of six and maximum of 72 hours then analyzed on a Shimadzu UV 1820 spectrophotometer at 540 nm.

Electrical conductivity and pH were measured using a 2:1 DI water:soil slurry based on a modified version of the methods described by Thomas (1996), and Smith and Doran (1996).

Particle-size analyses was performed using the pipet method (Soil Survey Staff 2014). The soils were first sieved to 2 mm, and the analysis is based on size fraction designations defined as sand (0.05 - 2.0 mm), silt (0.002 - 0.05 mm), and clay (< 2 μm). This included first oxidizing any SOM in the soils with 30-35% hydrogen peroxide in a hot-water bath. The oxidized soil samples were then subject to 16 hours on a reciprocal shaker with a solution of sodium hexametaphosphate (NaHMP; $(NaPO_3)_6$) and sodium carbonate (Na_2CO_3) dissolved in DI water to disperse the soil particles. The samples were then sieved to 0.047 mm to separate sand particles from the clay and silt, which was collected in a 1-L volumetric cylinder. After the clay and silt slurry within the volumetric cylinders equilibrated to room temperature, a stirring rod was used to disturb the suspensions in the cylinders and subsamples were taken at 4.5 hours at a depth of 6.21 cm and placed into tared beakers which were oven-dried to determine clay content. Silt was calculated by subtracting the clay and sand fraction from the weight of the soil sample after oxidation of SOM.

A general enzyme assay was performed using the fluorescein diacetate (FDA) hydrolysis method based on an approach by Green, Stott, and Diack (2006). This involved shaking the two subsamples of 0.4 g of air-dry soil for 3 hours on a reciprocal shaker using 30 ml of THAM buffer [tris (hydroxymethyl) aminomethane, $C_4H_{11}NO_3$] and 0.3 ml of FDA lipase substrate solution. One of the samples was the control and no FDA was added. The reaction was halted by pipetting 1.2 ml of acetone into the sample, centrifuged, and analyzed colorimetrically at 490 nm. The control absorbance was subtracted from the reacted sample absorbance to correct for background color.

After testing for carbonates using HCl (carbonate content was below detection limits), total carbon (C) and N were analyzed using dry combustion analysis with a Costech Elemental Combustion System (ECS 4010; Nelson & Sommers, 1996).

Particulate organic matter C and N were measured based on a method by Cambardella and Elliott (1992). This involved 10 g of air-dry soil being shaken overnight on a reciprocal shaker in a 5% sodium hexametaphosphate solution then sieved to 53 μm and collected. Once POM was collected, oven dried at 60 °C, and ball-milled, it was analyzed for total C and N to determine POM C and N using dry combustion analysis.

Orthophosphate was determined using the extraction method based on Olsen et al. (1954), modified by Gavlak et al. (2005). This involved extracting 1.5 g of air-dry soil sieved to 2 mm with 30 mL 0.5 N sodium bicarbonate ($NaHCO_3$) adjusted to pH 8.5 with 2 M NaOH which was shaken for 30 minutes on a reciprocal shaker and filtered through Q5 filter paper. These extracts were then colorimetrically analyzed using a method first described by Watanabe and Olsen (1965) and modified by Gavlak et al. (2005). First, extracts were reacted with reagent A, comprised of ammonium molybdate ($C_{23}H_{33}ClMoN_4O_4$) and antimony potassium tartrate ($C_8H_4K_2O_{12}Sb_2$) dissolved in DI water. The solution was then added to a solution of diluted sulfuric acid (H_2SO_4). Followed by a reaction using reagent B comprised of ascorbic acid ($C_6H_8O_6$) dissolved into a subsample of the reagent A. After the addition of reagent B, the solution reacted for 30 minutes and up to two hours, before the absorbance was measured colorimetrically at 882 nm.

Both sodium pyrophosphate extractable iron and sodium dithionite extractable iron were determined. The sodium pyrophosphate extraction method as described by McKeague (1967) involved 0.4 g of air-dried soil sieved to 2 mm extracted with 40 mL of 0.1 M sodium

pyrophosphate ($Na_4O_7P_2$) solution into 50-mL centrifuge tubes. After shaking for 16 hours on a reciprocal shaker, the samples were centrifuged, then analyzed using methods adapted from Dominik and Kaupenjohann (2000) which involved one set of samples reacted with reagent A, which was composed of Ferrozine ($C_{20}H_{12}N_4Na_2O_6S_2$), ammonium acetate ($C_2H_7NO_2$), and ascorbic acid in DI water. The second set of samples was analyzed using reagent B, which is the same as reagent A, but without the Ferrozine added. These were the control samples and were subtracted from the Ferrozine reacted samples. All samples were then treated with 6 M HCl. Once reagents were added, the samples were allowed to react for 1.5 hours prior to colorimetric analysis at 565 nm. Sodium dithionite ($Na_2O_4S_2$) extractable iron was extracted using methods described by Mehra and Jackson (1958), adapted by Holmgren (1967) and Dominik and Kapenjohann (2000). 0.4 g air-dried soil sieved to 2 mm were extracted with 40 ml of a 0.3 M sodium citrate solution, followed by an addition of $Na_2O_4S_2$ to each sample. After 16 hours on a reciprocal shaker, samples were centrifuged and pipetted into cuvettes with the same reagent containing Ferrozine described above and allowed to react for 1.5 hours before being analyzed colorimetrically at 565 nm.

Determination of cation content (calcium, magnesium, potassium, sulfur, and sodium) utilized a method described by Helmke and Sparks (1996) and modified by Gavlak, Horneck and Miller (2005). 2 g of air-dried soil sieved to 2 mm was extracted in 50-mL centrifuge tubes with 20 mL of 1-M ammonium acetate with pH adjusted to 7.0, and then filtered. Just prior to analysis, 5 mL of soil extract and 5 mL of 2-ppm cesium chloride solution were combined in ICP analysis tubes. Extracts were then analyzed using an ICP OES Spectrometer (Thermo Scientific iCap 7000).

Permanganate oxidizable carbon was analyzed using a method described by Culman, Freeman, and Snapp (2012a, 2012b). 2.5 g of air-dried soil sieved to 2 mm was placed into 50-mL centrifuge tubes with 20 ml of potassium permanganate ($KMnO_4$) and calcium chloride ($CaCl_2$) solution with the pH adjusted to 7.02. Samples were shaken on a reciprocal shaker for 2 minutes, let settle for 10 minutes, and then centrifuged and diluted, followed by colorimetric analysis at 550 nm.

Soil organic matter content was calculated by multiplying total C content, measured via dry combustion analysis, by a factor of 2 (Pribyl 2010), which is based on the finding that SOM has a C content of 50%.

Statistical Analyses

All statistical analyses were performed using Microsoft Excel and R Software with user-interface R-Studio (v. 1.3.1093). Outliers were removed from the N_{min} dataset. These were calculated by first normalizing and converting each value to a proportion of the mean for each sampling date and moisture treatment at each site. Then, outliers were removed if they were more than three times the sampling year's interquartile range above or below the first quartile or third quartile based on a recommendation from Tukey (1977).

The collected soil data was subjected to a Principal Component Analysis (PCA) to determine contributions to the total variation of the dataset. The PCA was followed by a Pearson Correlation test, which determines the strength of a linear relationship between variables. Finally, the measured variables were subjected to stepwise linear regression to determine the strongest N_{min} predictor variables in this dataset. For multivariate regression analysis, first a linear model was built using the lm() function and then an Olsen stepwise regression was

applied using ols_step_both_p() function from the olsrr (version 0.5.3) package. Candidate variables were included or excluded according to their P-values. Variables with $P < 0.10$ were included, while those with $P > 0.30$ were excluded.

For the PCA, Pearson correlation test, and multivariate linear regression analysis, the average disturbed N_{min} data was used for each site.

N_{min} Data was log-transformed to correct for any issues of heteroscedasticity. Residuals vs. fitted Q-Q plots were used to test if assumptions were met.

For simple means comparisons, a paired T-Test was used. To test for interactions and treatment effects in the crop residue experiments, analysis of variance was used. This was then followed by either a Tukey Test or Dunnett method "control vs. treatment" pairwise comparisons.

For regional model validation, we utilized a model from Miller et al. (2018). Their study utilized many of the same analyses as our study, and also was developed for the same region.

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

$$(R^2 = 0.604)$$

(Eqn. 2, Miller et al. 2018)

Wherein the model parameters are defined by the following abbreviations: TC = total C (%), silt = proportion of silt, and FDA = fluorescein diacetate hydrolysis (mg FDA kg^{-1} oven-dry soil hr^{-1}).

Table 3.2: Abbreviations and units for all soil properties measured and reported. N_{min} corresponds to nitrogen mineralization. Units of mg N kg^{-1} OD soil include the sum of ammonium-N (NH_4^+-N) and nitrate (NO_3^--N).

Soil Property	Abbreviation	Units
Water Holding Capacity	WHC	g H_2O g^{-1} OD soil
Bulk Density	Pd	g cm^{-3}
Proportion of Sand	X.sand	Percent (%)
Proportion of Silt	X.silt	Percent (%)
Proportion of Clay	X.clay	Percent (%)
Electrical Conductivity	EC	µS cm^{-1}
C:N Ratio	C:N	NA
Total Nitrogen	Total N	Percent (%)
Total Carbon	Total C	Percent (%)
Orthophosphate	Olsen P	mg PO_4-P kg^{-1} OD soil
Ammonium Acetate Extractable Potassium	K	mg K kg^{-1} OD soil
Ammonium Acetate Extractable Calcium	Ca	mg Ca kg^{-1} OD soil
Ammonium Acetate Extractable Magnesium	Mg	mg Mg kg^{-1} OD soil
Ammonium Acetate Extractable Sulfur	S	mg S kg^{-1} OD soil
Dithionite Extractable Iron	FeD	mg FeD kg^{-1} OD soil
Pyrophosphate Extractable Iron	FeP	mg FeP kg^{-1} OD soil
Fluorescein Diacetate Hydrolysis	FDA	mg FDA kg^{-1} OD soil hr^{-1}
Microbial Biomass Carbon	MBC	mg C kg^{-1} OD soil
Permanganate Oxidizable Carbon	POXC	mg POXC kg^{-1} OD soil
Particulate Organic Carbon	POC	mg POC kg^{-1} OD soil
Particulate Organic Nitrogen	PON	mg PON kg^{-1} OD soil
Initial Soil Mineral Nitrogen Content	Initial N	mg N kg^{-1} OD soil
Disturbed N_{min} at Field Moisture	IncNFM	mg N kg^{-1} OD soil
Disturbed N_{min} at 60% WHC	IncN60	mg N kg^{-1} OD soil
Undisturbed Core N_{min}	Core N	mg N kg^{-1} OD soil

3.3 Results

Soil Properties in the 17 Field Sites Sampled

Abbreviations and units are shown in Table 3.2. The soil summary data is shown in Figure 3.1 in the Materials and Methods. Electrical conductivity (EC) across sites had

considerable variation, ranging from 64 µS cm^{-1} up to 1454 µS cm^{-1}. With a general trend of increasing EC the further south the sites were located (Figure 3.1). Initial mineral N also tended to increase the further south the sites were located and ranged from 1.3 to 35.7 mg N kg^{-1} OD soil across all sites (Table 3.3). There was a wide range of textures across the sites, with the percent sand (X.sand) ranging from 1.1% to 90.0% and percent clay (X.clay) ranging from 3.7% to 55.6%.

Soil organic matter related results can be found in Table 3.3 and Figure 3.1. Total C ranged from to 0.32% to 1.4%, with an average of 0.94%. Total N ranged from 0.03% to 0.15%, to with an average of 0.11%. Soil organic matter ranged from 0.6% to 2.9%. Microbial biomass C (MBC) ranged from 85 to 316 mg C kg^{-1} OD soil, with an average of 214 mg C kg^{-1} OD soil. Particulate organic C (POC) ranged from 792 to 2,866 mg POC kg^{-1} OD soil, with an average of 1,698 mg POC kg^{-1} OD soil. Particulate organic N (PON) ranged from 79 to 291 mg PON kg^{-1} OD soil, with an average of 155 mg PON kg^{-1} OD soil.

Table 3.3: Soil organic matter related results (next page). Site names indicate first letter of county name, followed by that site's sampling number (C = Colusa, F = Fresno, S = Stanislaus, Y = Yolo). The parenthesized numbers to the right of each value indicate standard deviations. Abbreviations can be found in Table 3.2. All the analyses were performed on air-dried soil, with the exception of MBC and Initial N, collected in the top 15 cm of the soil profile after removal of the dry topsoil.

Site	Total C (%)		Total N (%)		C:N Ratio		MBC (mg MBC kg^{-1} OD soil)		FDA (mg FDA kg^{-1} OD soil hr^{-1})		POXC (mg POXC kg^{-1} OD soil)		POC (mg POC kg^{-1} OD soil)		PON (mg PON kg^{-1} OD soil)		Initial N (mg N kg^{-1} OD soil)	
C1	0.78	(0.03)	0.08	(0.003)	9.4	(0.2)	174.4	(29.9)	8.8	(2.2)	308	(36)	2795	(1366)	291	(148)	5.0	(0.69)
C2	1.44	(0.02)	0.13	(0.001)	10.7	(0.1)	315.6	(31.4)	17.5	(4.0)	506	(19)	1951	(233)	105	(9)	1.3	(0.35)
C3	1.32	(0.05)	0.14	(0.004)	9.5	(0.1)	241.5	(31.5)	11.4	(2.2)	500	(11)	2073	(404)	134	(21)	7.3	(0.53)
C4	0.84	(0.06)	0.10	(0.009)	8.3	(0.2)	174.9	(46.1)	11.9	(2.8)	284	(31)	1684	(343)	177	(23)	16.3	(5.59)
C5	0.92	(0.03)	0.11	(0.006)	8.1	(0.3)	205.7	(32.4)	15.2	(2.0)	334	(15)	1788	(935)	222	(110)	8.5	(1.44)
C6	1.44	(0.49)	0.15	(0.047)	9.5	(0.4)	141.2	(27.4)	19.0	(1.8)	467	(29)	1727	(695)	152	(49)	8.3	(2.36)
F1	0.74	(0.03)	0.08	(0.004)	8.9	(0.4)	239.0	(64.1)	10.7	(3.4)	239	(45)	1704	(390)	168	(57)	16.4	(3.28)
F2	0.87	(0.01)	0.10	(0.002)	9.2	(0.1)	230.5	(43.8)	7.9	(1.3)	272	(17)	1248	(116)	111	(6)	35.7	(4.29)
S1	0.32	(0.07)	0.03	(0.006)	9.5	(0.7)	85.0	(18.9)	4.1	(0.9)	157	(42)	1664	(973)	150	(109)	4.2	(0.55)
S2	1.04	(0.01)	0.12	(0.002)	8.4	(0.1)	214.4	(17.2)	8.6	(1.0)	319	(70)	1217	(623)	127	(87)	20.7	(4.00)
S3	0.86	(0.05)	0.11	(0.005)	7.7	(0.1)	188.9	(44.7)	10.2	(1.1)	234	(15)	1093	(622)	110	(38)	12.3	(2.83)
S4	0.94	(0.04)	0.12	(0.005)	7.8	(0.1)	263.8	(63.2)	10.2	(0.6)	257	(36)	857	(142)	97	(8)	16.3	(5.86)
S5	0.81	(0.06)	0.10	(0.005)	8.5	(0.2)	200.7	(38.1)	16.0	(1.9)	292	(88)	2866	(654)	290	(70)	9.8	(1.03)
Y1	0.98	(0.01)	0.11	(0.001)	9.0	(0.1)	294.2	(34.1)	15.0	(1.3)	330	(17)	2071	(467)	146	(57)	5.7	(0.72)
Y2	0.86	(0.05)	0.10	(0.002)	8.8	(0.6)	283.8	(48.6)	18.5	(3.1)	355	(33)	2286	(301)	172	(6)	3.6	(0.45)
Y3	0.90	(0.03)	0.10	(0.005)	9.3	(0.2)	180.2	(29.5)	6.2	(1.9)	295	(26)	1055	(557)	110	(62)	9.1	(4.41)
Y4	0.93	(0.02)	0.10	(0.005)	9.3	(0.3)	198.1	(20.6)	6.9	(1.4)	298	(34)	792	(240)	79	(16)	5.3	(0.81)

Plant available macro and micronutrients, which we refer to as soil mineralogical data, can be found in Table 3.4. Pyrophosphate extractable Fe (FeP) ranged from 35 to 835 mg FeP kg^{-1} OD soil, with an average of 303 mg FeP kg^{-1} OD soil. Dithionite extractable Fe (FeD) ranged from 2,355 to 15,119 mg FeD kg^{-1} OD soil, with an average of 11,266 mg FeD kg^{-1} OD soil. Ammonium acetate extractable Mg ranged from 62 to 2,158 mg Mg kg^{-1} OD soil, with an average of 986 mg Mg kg^{-1} OD soil.

Table 3.4: Mineralogical analyses results. This table features plant-available macro and micronutrient concentrations. Site names indicate the first letter of the county name, followed by that site's sampling number (C = Colusa, F = Fresno, S = Stanislaus, Y = Yolo). The parenthesized numbers indicate standard deviations. Abbreviations can be found in Table 3.2. All analyses were performed on air-dried soil collected in the top 15 cm of the soil profile after removal of the dry topsoil.

Site	FeP (mg FeP kg^{-1} OD soil)		FeD (mg FeD kg^{-1} OD soil)		K (mg K kg^{-1} OD soil)		Ca (mg Ca kg^{-1} OD soil)		Mg (mg Mg kg^{-1} OD soil)		S (mg S kg^{-1} OD soil)		Olsen P (mg PO_4-P kg^{-1} OD soil)	
C1	232	(14)	8206	(161)	116	(18.2)	2028	(128.0)	461	(46.5)	44.3	(14.0)	33.9	(5.2)
C2	748	(9.0)	14811	(155)	259	(35.0)	3870	(260.7)	2158	(130.7)	27.8	(16.7)	61.2	(6.3)
C3	835	(236)	13437	(111)	163	(33.2)	3663	(1073.5)	1593	(770.9)	22.6	(14.6)	57.8	(14.1)
C4	198	(18)	9354	(36)	109	(22.1)	2671	(156.5)	684	(60.7)	29.1	(1.1)	40.9	(9.2)
C5	546	(56)	9443	(57)	281	(54.1)	2237	(171.3)	655	(37.6)	27.2	(4.9)	100.3	(22.1)
C6	820	(90)	10446	(107)	144	(16.6)	2667	(179.2)	785	(59.2)	49.6	(8.2)	55.3	(50.2)
F1	37	(2.0)	12980	(3202)	205	(18.2)	4554	(367.9)	506	(21.2)	517.2	(407.5)	10.3	(1.4)
F2	35	(3.4	12321	(373)	403	(25.6)	5454	(108.7)	507	(19.5)	201.1	(24.6)	7.6	(2.3)
S1	117	(11)	2355	(474)	103	(18.1)	463	(45.4)	62	(7.0)	2.8	(0.6)	34.4	(2.5)
S2	110	(5.3)	13348	(357)	354	(46.2)	2220	(135.7)	846	(73.5)	42.8	(3.5)	81.6	(15.2)
S3	100	(3.0)	13263	(211)	220	(33.4)	2786	(295.3)	1285	(134.0)	37.8	(4.2)	28.8	(7.8)
S4	73	(8.5)	13200	(185)	276	(10.4)	2376	(173.6)	1330	(122.1)	36.4	(4.6)	47.8	(5.0)
S5	547	(13)	3055	(112)	376	(77.1)	785	(67.7)	131	(20.4)	8.7	(0.8)	88.6	(9.5)
Y1	221	(8.3)	15119	(400)	190	(10.5)	2952	(71.6)	1796	(45.6)	21.5	(0.4)	3.5	(1.0)
Y2	325	(56)	10747	(204)	211	(41.4)	1403	(268.9)	692	(125.6)	13.3	(2.3)	34.3	(12.5)
Y3	97	(3.4)	14669	(113)	369	(17.0)	1681	(58.1)	1487	(58.5)	14.3	(3.8)	23.7	(3.4)
Y4	103	(5.0)	14772	(184)	445	(65.2)	2079	(337.1)	1788	(266.0)	15.7	(2.8)	20.4	(7.5)

Principal Component Analysis Results

A principal component analysis (PCA) was used to visualize and interpret the collected soil data. The first two principal components (PC) comprised 60.2% of the variation in the dataset (Figure 3.2). Textural and mineralogical variables were dominant in the first principal component (PC1, 35.9%). Driven largely by X.sand, FeD, X.clay, and Pd, which comprised 10.1%, 8.7%, 7.8%, and 7.2% of PC1, respectively. This was supported by a significant correlation between all four of these variables (Figure 3.3). For the second principal component (PC2, 24.3%), the variables that contributed the most were FeP and FDA hydrolysis, which comprised 12.0% and 11.1% of PC2, respectively. This was also supported by a significant correlation between these two variables.

All N_{min} related variables were clustered in the top right quadrant together (IncNFM, IncN60, and CoreN) (Figure 3.2). Surrounding the N_{min} cluster, the variables PON, POC, and OlsenP were also found. The sites that had the most influence in that cluster included C1, C4, C5, S5, and Y2. All of these sites were ranked in the top five for all variables in that cluster, with the exception of C1, C4, and Y2 for OlsenP, C4 and C5 for POC, and C5 for IncNFM.

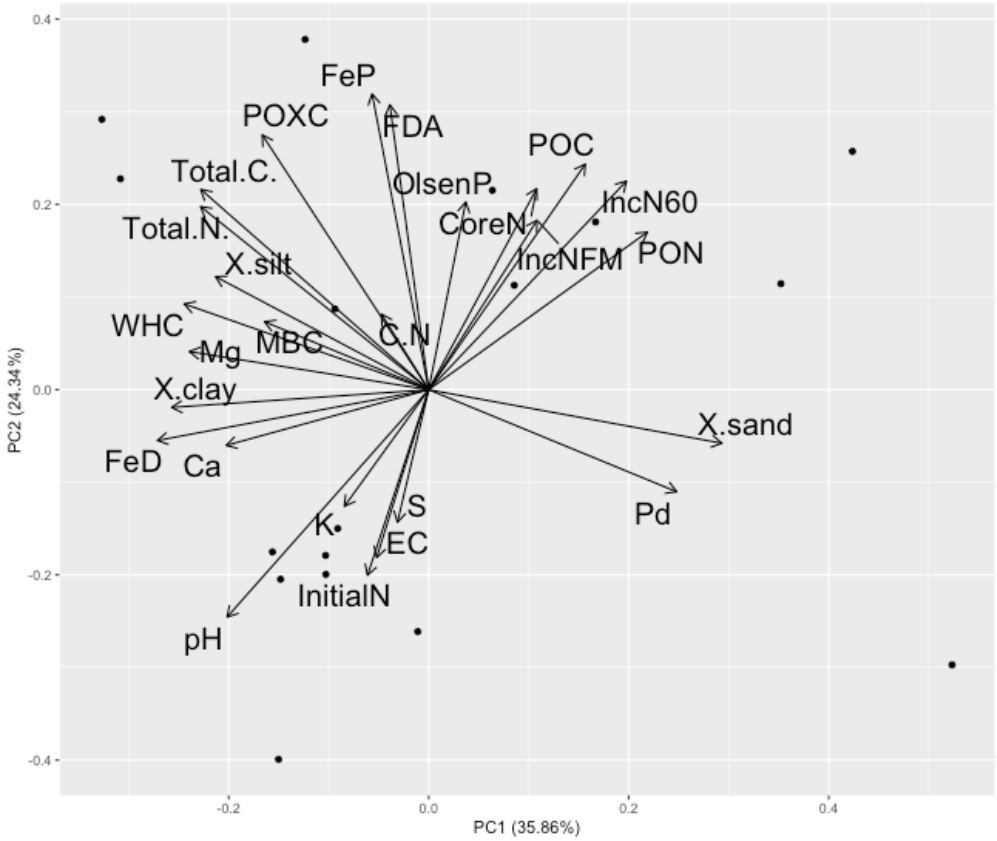


Figure 3.2: Principal component analysis. Features principal component 1 (PC1, 35.9%) and 2 (PC1, 24.3%) (n = 17). Arrows indicate which measured variable is contributing to that PC. For abbreviations see Table 3.2 (n = 4). All analyses were performed on soil samples collected from the top 15 cm of the soil profile after removal of the dry topsoil.

Pearson Correlation Matrix Results

All N_{min} related variables (IncNFM, IncN60, and Core N) share significant positive correlations to POC, PON, and FDA hydrolysis and significant negative correlation to pH (Figure 3.3). Both IncN60, and Core N show a significant negative correlation with X.clay. While IncN60 exhibits significant negative correlations with Mg and FeD (Figure 3.3).

Particulate organic N had significant negative correlations with X.clay, pH, Mg, and FeD. As well a corresponding positive correlation with X.sand (Figure 3.3).

Several variables, namely total N, total C, Ca, Mg, FeD, and POXC all showed positive significant correlations with WHC, and significant negative correlations with Pd, and X.sand (Figure 3.3). With all but POXC also sharing a significant positive relationship with X.clay.

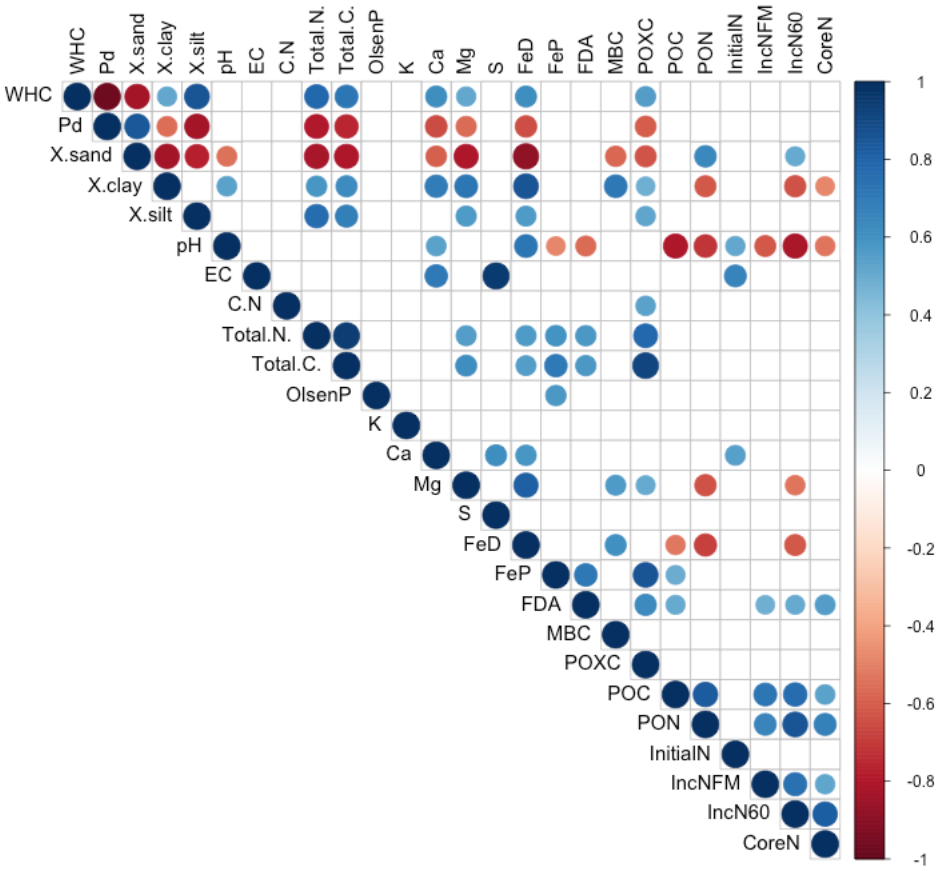


Figure 3.3: Pearson's correlation matrix. The matrix features all measured soil property variables including the average incubation N mineralization (N_{min}) data and how they relate to each other in their variability (n = 17). Significant correlations indicated with increased circle size and color saturation (positive correlations shown in blue and negative shown in red). No

circle indicates insignificant correlation (P > 0.05). For abbreviations see Table 3.2. All the analyses were performed on soil collected from the top 15 cm of the soil profile.

Determining the Controlling Factors on Soil N_{min} in the Central Valley using Multivariate Stepwise Linear Regression Analysis

To establish the soil properties that determine N_{min} in the undisturbed soil cores, multiple stepwise linear regression was performed with all the measured soil property variables and average Core N incubation data, resulting in Equation 1.

$$\text{Core N} = (0.1085)\text{PON} + (0.2906)\text{X.silt} - 2.8235 \quad \text{(Eqn. 1)}$$

$$\text{Adjusted-}R^2 = 0.65,\ P < 0.05$$

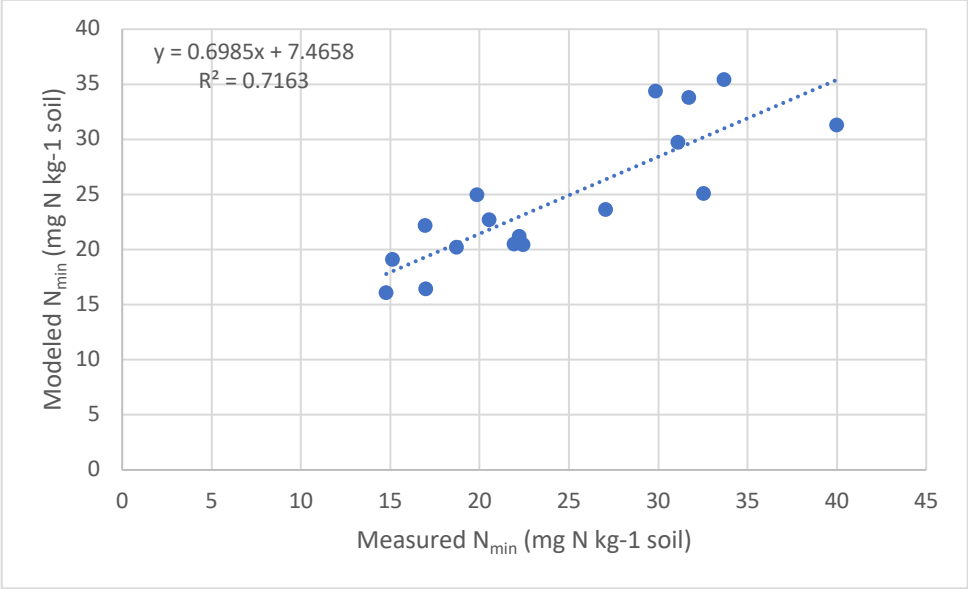


Figure 3.4: Measured versus modeled undisturbed core (Core N) N mineralization (N_{min}) using Equation 1 for all sites. Undisturbed cores (n = 17) were incubated for 10 weeks at 60% WHC and 25 ºC. Modeled N_{min} was calculated based on Equation 1 (adjusted $R^2 = 0.65$, P <

0.05). The units for N_{min} (mg N kg^{-1} soil) correspond to the increase in soil mineral N (sum of ammonium-N and nitrate-N). Cores were collected from the top 15 cm of the soil profile after removal of dry topsoil.

Equation 1 featured PON and silt content as the variables included with an adjusted-R^2 of 0.65. With PON describing 46% of the variability in Core N. After performing stepwise linear regression for the disturbed potential $N_{min,}$ which was calculated by taking the average N_{min} across all sampling dates and is represented by IncN60, it was found that PON was also significant and explained over 72% of the variability in that set of N_{min} data averaged over the growing season ($P < 0.05$, Figure 3.5).

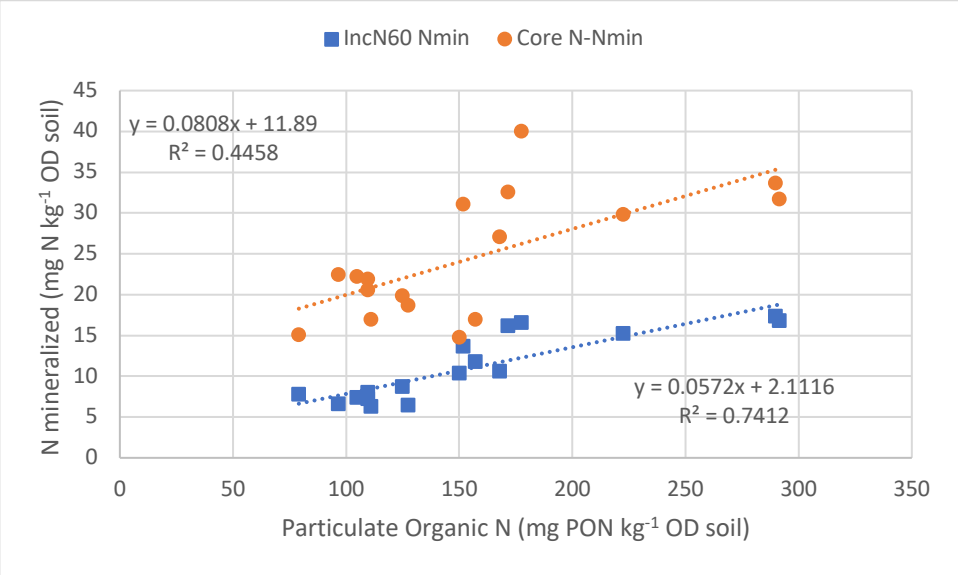


Figure 3.5: A comparison of particulate organic N (PON) with both undisturbed core (Core N) N mineralization (N_{min}) and disturbed 60% WHC (IncN60) N_{min} for all sites. Orange data points correspond to the average Core N-N_{min} and the blue squares correspond to the average IncN60 N_{min} of all the sampling dates ($n = 17$, $P < 0.05$). The units (mg N kg^{-1} soil) correspond

to the increase in soil mineral N (sum of ammonium-N and nitrate-N). Soils were collected from the top 15 cm of the soil profile after removal of the dry topsoil and incubated at ideal moisture and 25 ºC for ten and five weeks for the Core N and IncN60, respectively.

Comparing N_{min} Differences Between Undisturbed Soil Cores and Seasonal Disturbed Subsamples at 17 Sites

Nitrogen mineralized from the Core N during a ten-week incubation ranged from 14.8 to 40.0 mg N kg^{-1} OD soil (Table 3.5). The average N_{min} during the disturbed five-week IncN60 and IncNFM incubations for all sampling dates ranged from 6.3 to 17.4 mg N kg^{-1} OD soil, and 2.8 to 10.2 mg N kg^{-1} OD soil, respectively (Table 3.5).

Table 3.5: Incubation net N mineralization (N_{min}) results for three different treatments: disturbed field moist (IncNFM), 60% WHC (IncN60) and undisturbed core (Core N). This table displays the average N_{min} and standard deviation (SD) from the IncNFM, IncN60, and Core N incubations for each site. The IncNFM and IncN60 treatments were incubated for 5 weeks, while the Core N treatments were incubated for 10 weeks at 25 ºC. The IncNFM and IncN60 treatments display the average N_{min} of all the sampling dates. The units (mg N kg^{-1} soil) correspond to the increase in soil mineral N (sum of ammonium-N and nitrate-N). Soils were collected from the top 15 cm of the soil profile after removal of the dry topsoil. The letter designations in each column indicate significant differences according to Tukey's Test ($n = 4$, $P < 0.05$).

Site	IncNFM N_{min}	IncNFM N_{min} SD	IncNFM Letter (P<0.05)	IncN60 N_{min}	IncN60 N_{min} SD	IncN60 Letter (P<0.05)	Core N N_{min}	Core N N_{min} SD	Core N Letter (P<0.05)
C1	8.7	2.0	ef	16.8	1.5	e	31.7	5.3	abc
C2	4.2	1.1	abcd	7.4	1.2	a	22.2	6.7	abc
C3	3.2	1.0	abc	8.7	1.0	ab	19.9	3.1	ab
C4	6.7	1.2	cdef	16.5	4.0	e	40.0	10.2	c
C5	4.8	1.0	abcd	15.2	1.8	cde	29.9	6.1	abc
C6	5.6	1.3	abcde	13.6	1.3	bcde	31.1	1.4	abc
F1	6.1	0.9	abcde	10.6	1.6	abcd	27.1	13.8	abc
F2	2.8	0.8	ab	6.3	1.2	a	17.0	7.1	ab
S1	2.8	0.7	ab	10.4	1.5	abc	14.8	1.6	ab
S2	3.2	0.7	abc	6.4	1.4	a	18.7	2.4	ab
S3	2.8	0.4	ab	8.0	0.5	ab	21.9	6.0	abc
S4	3.1	0.4	ab	6.6	0.8	a	22.4	7.3	abc
S5	7.1	0.9	def	17.4	0.8	e	33.7	2.2	bc
Y1	10.2	3.9	f	11.8	4.3	abcde	16.9	7.1	ab
Y2	6.3	0.8	bcde	16.2	4.5	de	32.5	12.1	abc
Y3	2.5	0.7	a	7.2	2.1	a	20.5	10.8	ab
Y4	3.1	1.7	ab	7.8	2.4	a	15.1	1.9	a

Growing season N_{min} was highly variable across sites for both the IncNFM and IncN60 soil moisture treatments. Maximum, minimum, and average N_{min} across sites for the IncN60 soil moisture treatments were 39.1, 2.0, and 10.9 mg N kg^{-1} OD soil, respectively. The maximum, minimum, and average N_{min} across sites for the IncNFM treatments was 36.1, -0.2, and 4.9 mg N kg^{-1} OD soil, respectively. The average N_{min} across all sampling dates is shown in Table 3.5 for each site. We expected and observed that the IncNFM treatments generally mineralized less N than the IncN60 treatments. We anticipated that by holding soil moisture at 60% WHC, we would see a more constant N_{min} rate throughout the season, which was not always the case. At some sites we saw the expected response, with increasing moisture resulting in greater N_{min} and the IncN60 treatment leading to more consistent and stable N_{min} trends throughout the season (Figure 3.6). Site C6 provides a good example of this pattern (Figure 3.6, panel 1a and 1b). Generally, most sites lacked any predictable pattern among the IncNFM and IncN60 treatments throughout the season. Site S3 provides an example of the highly variable N_{min} pattern regardless

of soil moisture content (Figure 3.6, panel 2a and 2b). Conversely, other sites exhibited notable mirrored N_{min} trends between their IncNFM and IncN60 treatments, with both the treatments displaying shared increasing and decreasing net N_{min} at each sampling date, regardless of soil moisture content. An example is site F1 (Figure 3.6, panel 3a and 3b). However, at every site (with the exception of Y1) the IncNFM treatment mineralized significantly less than the IncN60 treatment (Figure 3.6, Table 3.5).

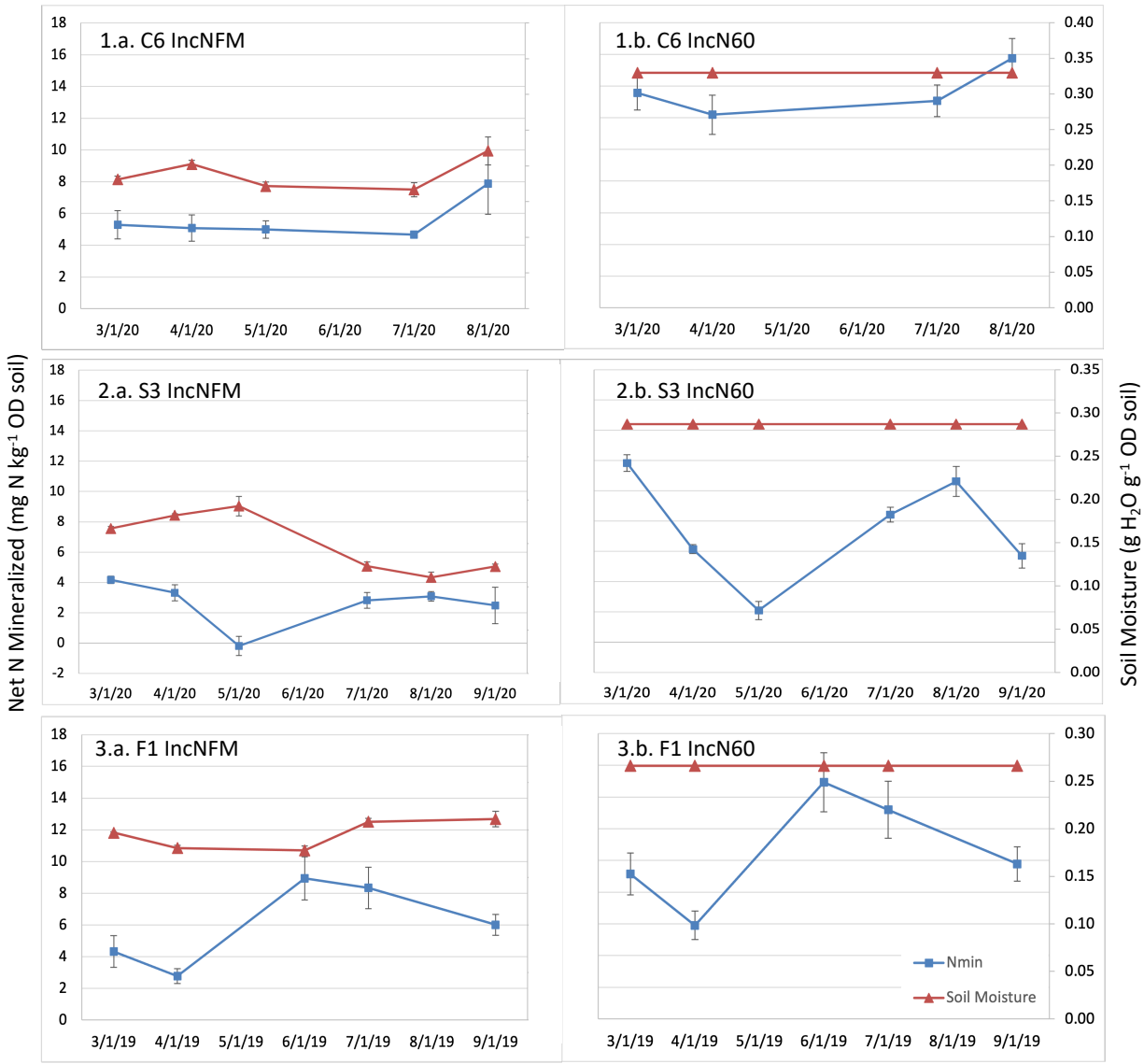


Figure 3.6: Regional seasonal net N mineralization (N_{min}) variability for three of seventeen sites. This figure displays seasonal N_{min} (mg N kg^{-1} OD soil) for multiple sampling dates at three sites: 1.) Colusa 6 (C6), 2.) Stanislaus 3 (S3), and 3.) Fresno 1 (F1); under two different soil moisture treatments: a.) field moisture (IncNFM, left column) and b.) 60% WHC (IncN60, right column). The error bars indicate standard error. The units (mg N kg^{-1} soil) correspond to the increase in soil mineral N (sum of ammonium-N and nitrate-N). All soils were collected from the top 15 cm of the soil profile after removing the dry topsoil and incubated at 25 ºC for five weeks (n = 4).

The average weekly net N_{min} for each treatment and site was used for the comparison between all incubation data, which included the Core N, IncN60 and IncNFM (Figure 3.7, Table 3.5). According to a Tukey pairwise comparison, the average IncN60 and Core N mineralized significantly more N per week than the average IncNFM treatments ($P < 0.05$, Figure 3.7). However, weekly Core N was not statistically different when compared to the average weekly IncN60 N_{min} (Figures 3.7 and 3.8).

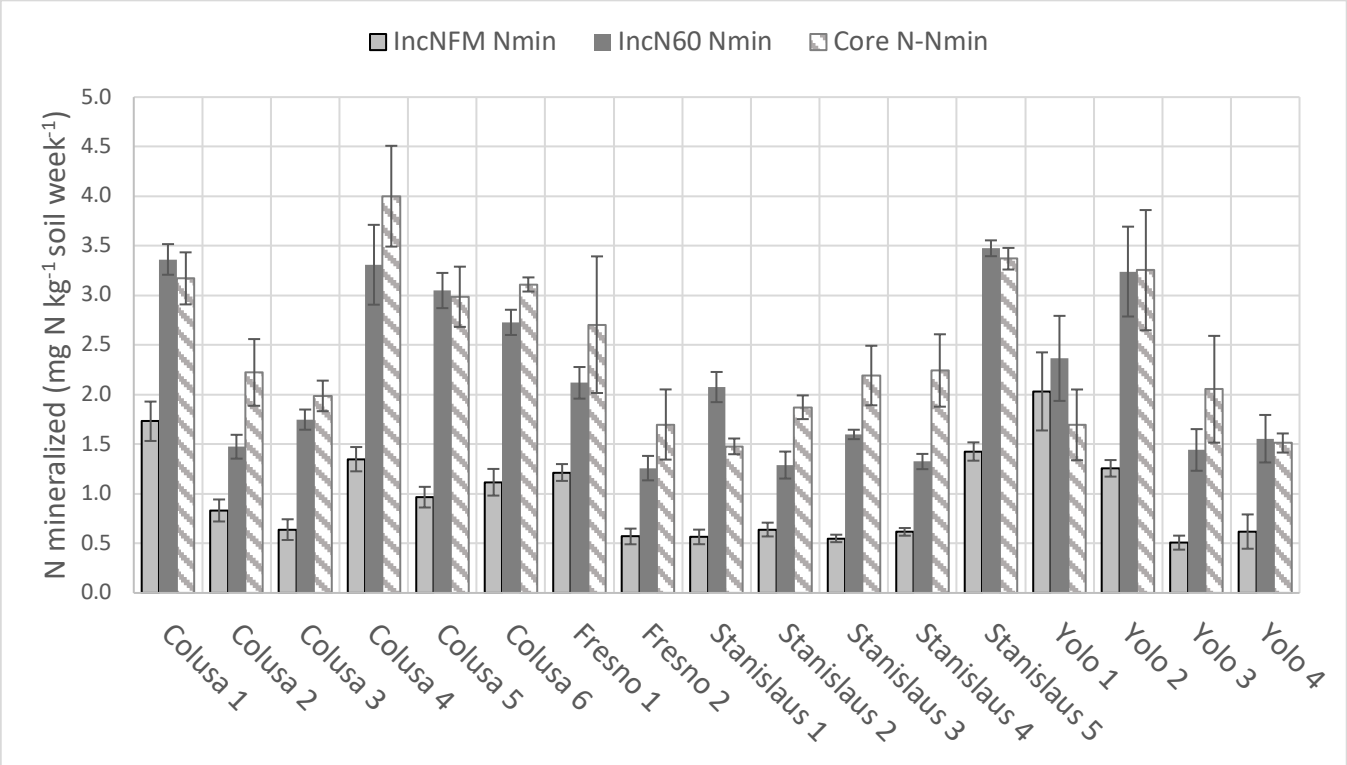


Figure 3.7: Average incubation N mineralization (N_{min}) on a weekly basis for three soil treatments: field moist (IncNFM), 60% WHC (IncN60), and undisturbed core (Core N) for all sites. The IncNFM treatments were incubated at field moisture, while the IncN60 and Core N treatments were incubated at the ideal moisture content and 25 ºC. The Core N treatments were incubated for 10 weeks, while the IncNFM and IncN60 treatments were incubated for five weeks. The IncNFM and IncN60 N_{min} data is the average of all sampling dates. The average N_{min} data was normalized to mg N kg^{-1} soil $week^{-1}$. The error bars represent standard error (n = 4). The units (mg N kg^{-1} soil $week^{-1}$) correspond to the increase in soil mineral N (sum of ammonium-N and nitrate-N). All soils were collected from the top 15 cm of the soil profile after removing the dry topsoil.

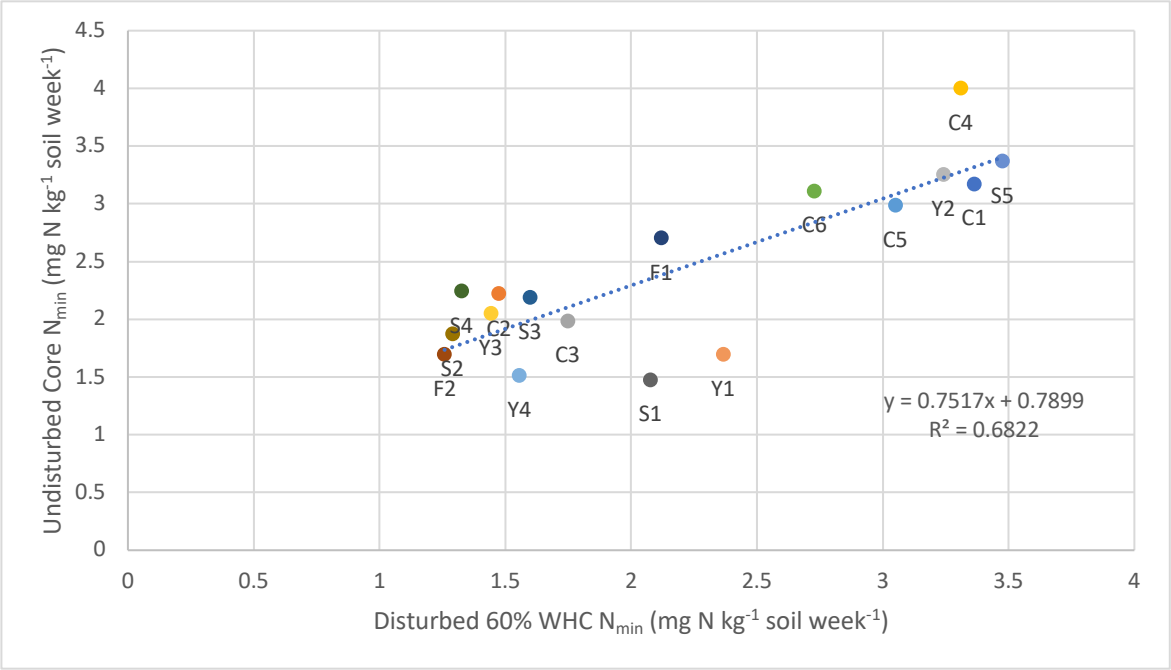


Figure 3.8: Weekly average disturbed 60% WHC (IncN60) N mineralization (N_{min}) and undisturbed core (Core N) N_{min} for all sites. This figure features the average N_{min} incubation data for all sites Core N and the average of all sites sampling dates for IncN60. The Core N treatments were incubated for 10 weeks, and the IncN60 treatments were incubated for five weeks. Both treatments were incubated at ideal moisture content and 25 ºC. The data was normalized to mg N kg^{-1} soil $week^{-1}$ and corresponds to the increase in soil mineral N (sum of ammonium-N and nitrate-N) (n = 17). All soils were collected from the top 15 cm of the soil profile after removing the dry topsoil.

Effects of Disturbance and Soil Moisture on N Mineralization in Soils from 17 Sites

One goal of the disturbed N_{min} incubations was to determine the effect of soil moisture on N_{min}. As 60% WHC is considered the ideal moisture content for N_{min} in most soil types, it was hypothesized that the IncN60 treatments would mineralize more N than the IncNFM treatments,

when the soil moisture content in the IncN60 treatments was greater than that of the IncNFM treatments (Kutlu et al. 2018). Using the average for each treatment across all sampling dates for each site, a Tukey test was used to test this hypothesis. We confirmed that the IncN60 treatments did mineralize significantly more N than the IncNFM treatments across sites, with an average difference across all sites of 6.1 mg N kg^{-1} OD soil in the IncN60 treatments ($P < 0.05$, Table 3.5). The same trend was observed at every site with the exception of Yolo 1 (Y1). Site Y1 was the only site within this dataset that did not have significantly increased N_{min} under the IncN60 treatment. It was also the most variable N_{min} data of all the sites (Table 3.5).

To assess the overall effect of soil moisture on N_{min}, the relative N_{min}, which is the IncNFM N_{min} expressed as a proportion of the potential IncN60 N_{min}, was calculated. There was a significant positive relationship between the proportion of WHC and relative N_{min} ($P < 0.05$) (Figure 3.9). We also observed a slight textural trend related to clay content, where increasing clay content resulted in generally greater relative N_{min} (Figure 3.9). This trend is likely due to the increased WHC associated with higher clay content.

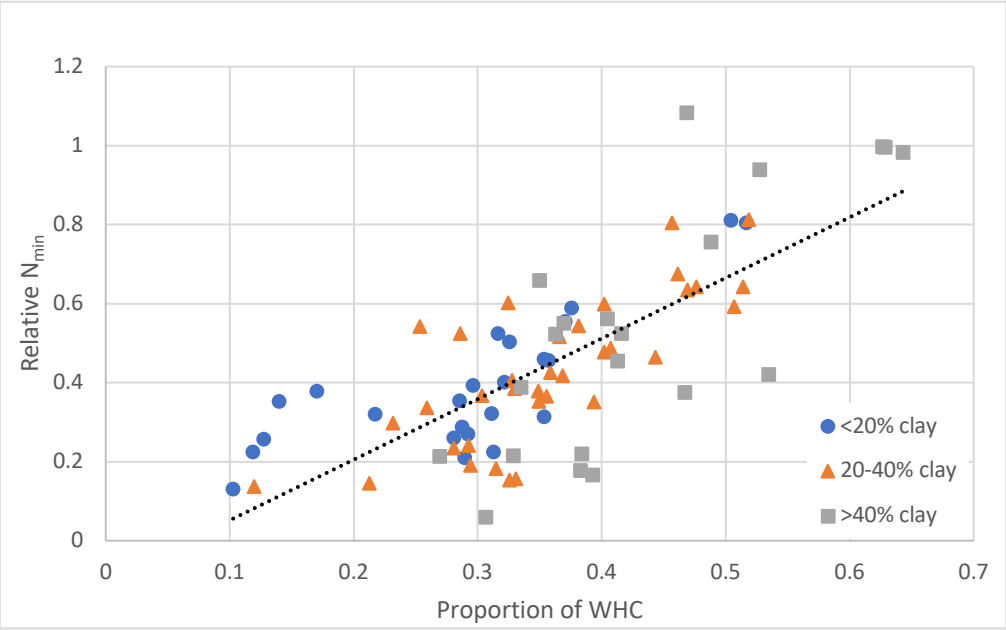


Figure 3.9: Relative N mineralization (N_{min}) at field moisture (FM) expressed as a proportion of water holding capacity (WHC) for all sites and sampling dates. Relative N_{min} was calculated as a proportion of potential N_{min} at 60% WHC (60%). (FM N_{min}) / (60% N_{min}) = Relative N_{min} (n = 80, adjusted-R^2 = 0.574, $P < 0.05$). The data was sorted by the percentage of clay (< 2 µm). Outliers were removed according to calculations described in the materials and methods (Tukey 1977). Soils were collected from the top 15 cm of the soil profile after removing the dry topsoil and incubated at 25 ºC for five weeks.

The Effects of the Previous Seasons Crop Residues on Undisturbed Core N_{min}

To investigate whether the previous seasons crop affected the pre-season undisturbed core N_{min}, Equation 1 was used in combination with data from a separate study we performed utilizing seven different residue treatments (see Chapter 4: Field Residue Trial). The residue study included an undisturbed core incubation from each of the residue treatment plots. We hypothesized that among each residue type would result in significantly different N turnover

trends, as well as when compared to the control (no residue treatment). The N_{min} data from our main study was combined with Equation 1 to determine if the same N_{min} or N immobilization trends observed in the residue trial were mirrored in our study's undisturbed core incubation (Chapter 4: Field Residue Trial: Figure 4.4). Of the crop residues studied in the residue trial, five were also the previous crops at our field sites, namely corn, watermelon, sunflower, processing tomatoes, and cotton. Most of the sites studied rotated annual crop types each growing season. Only six out of the 17 sites shared the same crop type from the previous growing season, with four out of those six growing tomatoes, and one growing cotton, and one growing melons (Table 3.1).

In the residue trial, the sunflower residue treatments mineralized the least N of all the residue treatments, thus overestimation of N_{min} was expected from sites where sunflower had been the previous crop (Chapter 4: Field Residue Trial: Figure 4.4). However, the predicted N_{min} for those sites was less than the measured N_{min}. With the other four crop types, the over or under prediction of N_{min} were inconsistent.

Overall, the mineralization and immobilization trends were not clear with the five residues shared between both trials. It was determined that the previous year's crop did not have a predictable effect on the observed undisturbed core N_{min} trends for the sites and crops included in our study (Figure 3.10).

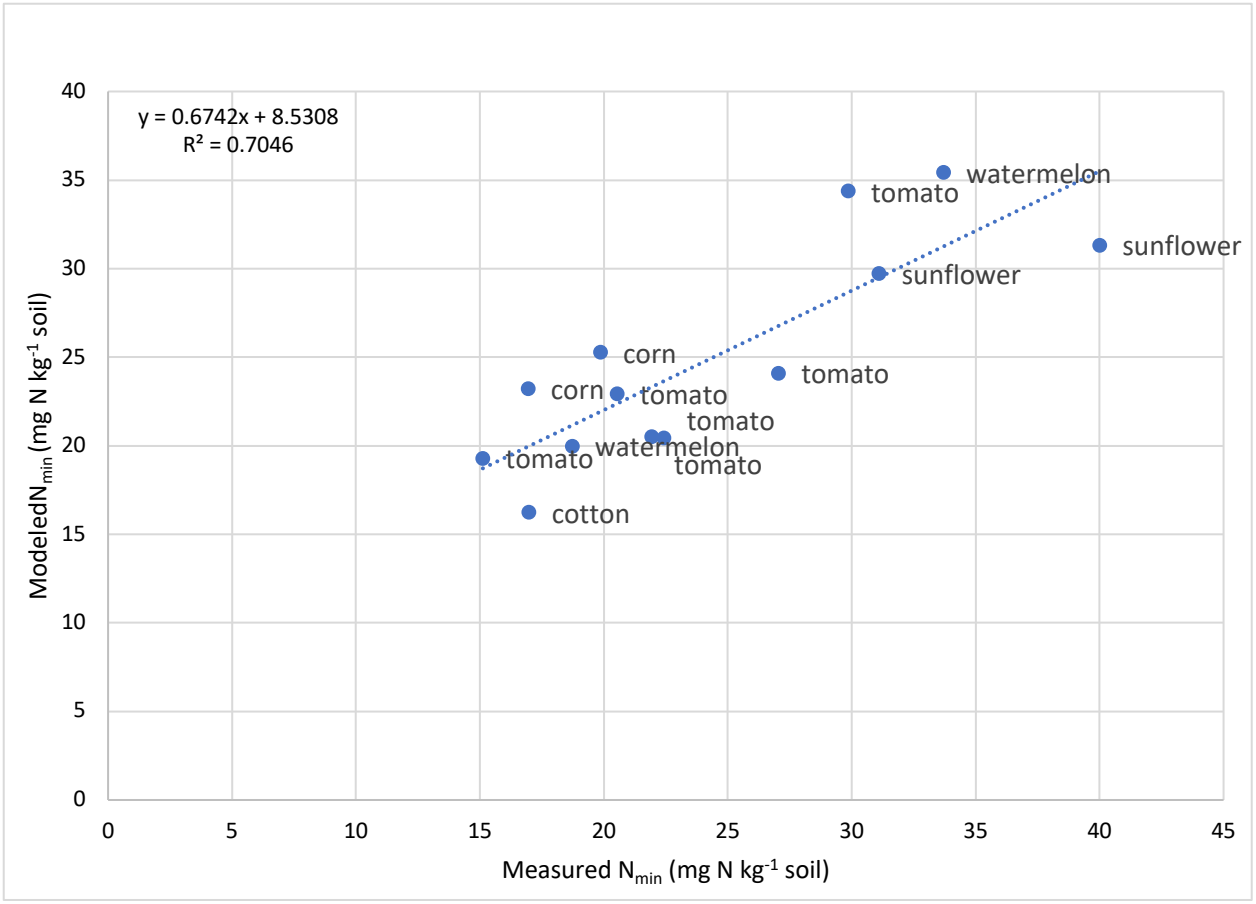


Figure 3.10: Modeled vs. measured undisturbed core (Core N) N mineralization (N_{min}) comparing the previous season's crop residues with trends from the residue trial in Chapter 4. Five crop residues were compared between our main study and the residue trial from Chapter 4 using Equation 1: CoreN = (0.1085)PON + (0.2906)X.silt – 2.8235 (n = 13). The labels correspond to the previous season's crop. The units (mg N kg^{-1} soil) correspond to the increase in soil mineral N (sum of ammonium-N and nitrate-N). Soil cores were collected from the top 15 cm of the soil profile after removing the dry topsoil.

Determining the Importance of Developed Roots on Seasonal N Mineralization

To determine any clear N_{min} trends throughout the growing season, we investigated whether the presence of an established root system significantly affected N_{min}. In our study, full canopy coverage, as observed when soil samples were taken, was used as a proxy for the presence of a fully developed root system. Then the IncN60 N_{min} data was divided into "pre-plant" and "mature plant" categories for each site and sampling date. All sampling dates categorized as "mature plant" were averaged for all the applicable dates.

A paired T-Test revealed there were no significant differences in N_{min} with or without the presence of a fully developed root system ($P > 0.05$; Figure 3.11). While the presence of roots resulted in potentially significant differences in N_{min} at some sites, there were no clear trends across all sites. Therefore, within this study, the presence of a fully established root system did not explain the seasonal IncN60 N_{min} trends observed.

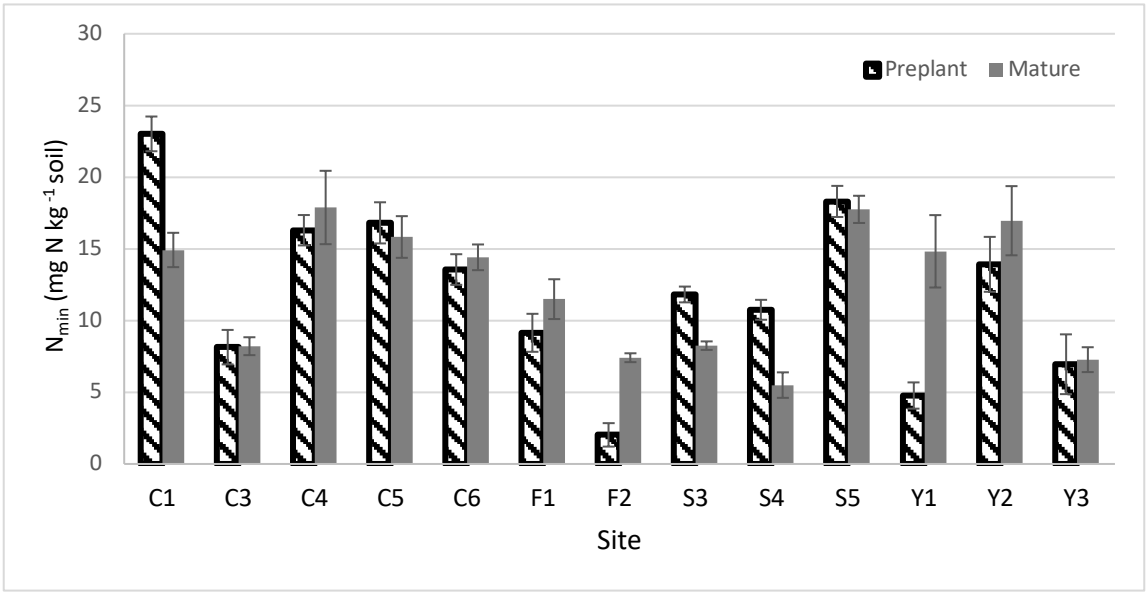


Figure 3.11: A comparison of N mineralization (N_{min}) for pre-plant vs. fully established root system (mature plant) at 60% WHC for all applicable sites. This figure features pre-

plant and mature plant N_{min} averaged by site (n = 13; paired T-Test P > 0.05). The units (mg N kg^{-1} soil) correspond to the increase in soil mineral N (sum of ammonium-N and nitrate-N). Soil samples were collected from the top 15 cm of the soil profile after removal of the dry topsoil. *Note: four out of seventeen sites were removed from this analysis due to missing data. Reasons for missing data were missing pre-plant N_{min} data, the site was fallow during the trial, or the N_{min} data was removed due to outliers.*

Regional Model Validation

To validate this study's Core N-N_{min} model, a separate independent dataset from Miller et al. (2018) was utilized. The study by Miller et al. (2018) developed an N_{min} model for soils with low SOM contents from the Sacramento and San Joaquin Valley (Eqn. 2) and utilized many of the same soil analyses as our study. The Miller et al. (2018) study's model included total C (TC), silt, and FDA hydrolysis. To compare Equations 1 and 2, the separate data sets were combined, tested and validated using each model (Figure 3.12).

When comparing modeled versus measured values of N_{min} with the combined dataset using Equation 1, the adjusted-R^2 was 0.28 ($P < 0.05$, Figure 3.12). However, when using the Miller et al. (2018) Equation 2, the resulting adjusted-R^2 was 0.41 ($P < 0.05$, Figure 3.12). The combined dataset included 53 total sites, with Miller et al. (2018) contributing 36 sites, and our dataset contributing 17 sites.

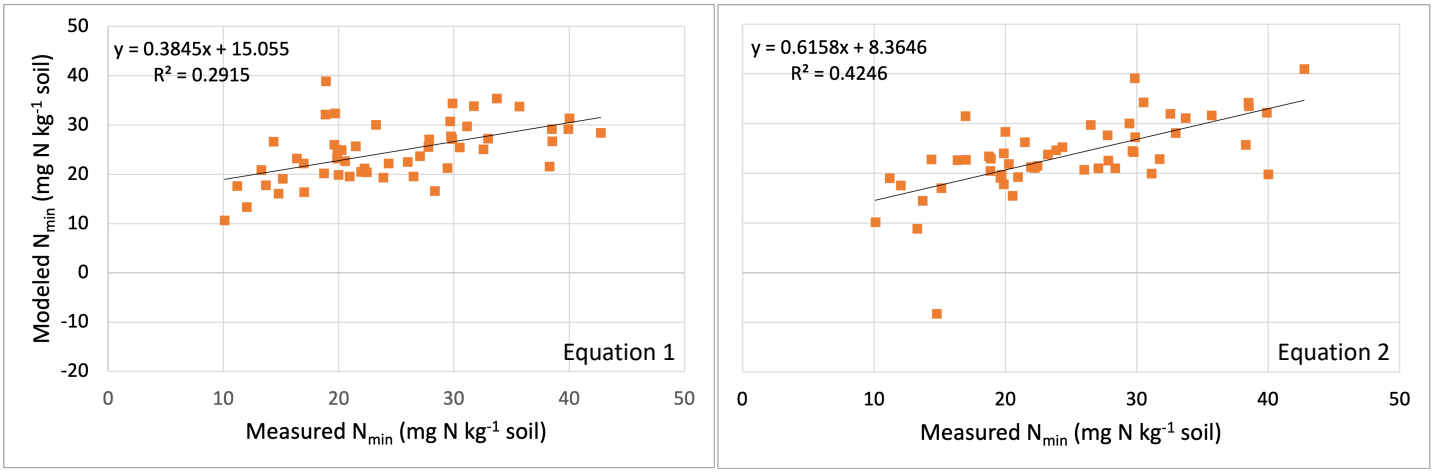


Figure 3.12: Modeled versus measured undisturbed core (Core N) N mineralization (N_{min}) featuring a combined dataset from Miller et al. (2018) and our study (n = 57). The Core N-N_{min} data was validated using Equation 1 from this study: Core N = (0.1085)PON + (0.2906)X.silt – 2.8235, and Equation 2 from Miller et al. (2018): N_{min} = - 44.82 + (12.79)TC - (0.610)TC^2 - (0.259)silt + (1.123)FDA. Both linear regressions resulted in $P < 0.05$. The units (mg N kg^{-1} soil) correspond to the increase in soil mineral N (sum of ammonium-N and nitrate-N). Soil cores were collected from the top 15 cm of the soil profile. *Note: (n = 17) for our study, and (n = 36) for the Miller et al. (2018) study*.

Table 3.6: Comparison between model variables in our study and the Miller et al. (2018) study. Maximum, minimum, and average values for particulate organic N (PON), silt, total C, and fluorescein diacetate hydrolysis (FDA) are included. These are the variables included in Equations 1 and 2. Soil was collected from the top 15 cm of the profile, after removing the dry topsoil. *Note: (n = 17) for this study, and (n = 36) for the Miller et al. (2018) study*.

Model Variables	Our Study			Miller et al. (2018) Study		
	Max	Min	Average	Max	Min	Average

PON (mg PON kg^{-1} OD soil)	291.44	79.11	155.42	296.45	51.08	146.15
Silt (%)	55.30	9.03	36.13	57.74	5.42	39.67
Total C (g C kg^{-1} OD soil)	14.44	3.18	9.41	15.31	5.95	10.27
FDA (mg FDA kg^{-1} OD soil hr^{-1})	19.23	3.91	11.60	33.58	3.38	14.56

3.4 Discussion

Exploration of Soil Properties in Relation to Modeling N Mineralization Utilizing Principal Component Analysis and Pearson Correlation Matrix

The PCA main contributing variables were X.sand, FeD, Pd, and X.clay for PC1, and FeP, and FDA hydrolysis for PC2.

All of the N_{min} related variables clustered in the top right quadrant and included IncNFM, IncN60, CoreN, and were surrounded by POC, PON, and Olsen P. The sites driving the cluster were C1, C4, C5, S5, and Y1.

Texture has been found in many studies as a leading variable determining N_{min} rates (Bechtold & Naiman, 2006; Cabrera et al. 2005; Colman & Schimel, 2013; Martínez et al. 2018; Miller et al. 2018; Wade et al. 2018). Sand content specifically has been found in other studies to be an important factor in predicting N_{min} (Martínez, Galatini, & Duval 2018). Interestingly, no textural variables were found in the N_{min} cluster. However, the Pearson Correlation Matrix showed significant negative correlations between X.clay and IncN60 and CoreN, and a weak positive correlation between IncN60 and X.sand.

Dithionite extractable iron (FeD) was not found in the N_{min} cluster of the PCA, though it did have a significant negative correlation with IncN60 in the Pearson Correlation Matrix. FeD is a measure of crystalline iron oxides and is likely an artifact of the pedological formation of the soil (McKeague, Brydon, & Miles 1971). Bullard (2012) found in their study of serpentinitic

California soils that increased levels of FeD was strongly associated with highly weathered soils. Texture, Pd, and FeD are all soil parameters mainly determined by soil formation and climate.

Pyrophosphate extractable iron (FeP) represents complexed amorphous organic Fe (McKeague, Brydon, & Miles 1971). This is reflected in the Pearson correlation matrix where FeP is significantly associated with total C. However, it was not significantly associated with any of the N_{min} variables. While FeP was found to be a main contributor to PC2, it was not located near the N_{min} cluster of the PCA. Miller et al. (2018) found FeP to be an important variable in their strongest N_{min} prediction model across high and low SOM containing soils. Various forms of Fe have been previously linked as important determining factors in other N_{min} prediction models (Miller et al. 2018; Wade et al. 2018). While our study's best fit model for predicting N_{min} did not include an Fe fraction, Fe has been implicated as an important variable contributing to the stabilization of SOM (Jilling et al. 2018).

The broad enzymatic analysis FDA hydrolysis is considered a proxy for microbial activity in soils (Miller et al. 2018). It is related to other biological assays which gauge SOM availability and quality such as POM or POXC (Miller et al. 2018). In the Pearson correlation matrix, FDA hydrolysis, POC, and POXC have a significant positive correlation. While FDA hydrolysis was not selected for the best fit model in this dataset, nor was it included in the N_{min} cluster in the PCA, it did have a significant relationship with all three N_{min} variables (IncNFM, IncN60, and CoreN) according to the Pearson correlation matrix (Figure 3.3). This could be due to effects previously described by Jilling et al. (2018), where the authors theorized that sorption of SOM to clay surfaces caused an increase in enzymatic activity due to the protection from fluctuating pH, temperature, ionic strength the mineral surfaces provided.

The Role of Particulate Organic N and Silt in Central Valley N Mineralization

Particulate Organic N

Particulate organic N (PON) and percent silt (% silt) were included in the best fit model for Core N (eqn. 1). This confirmed our hypothesis (1) that the best fit model would include a textural and SOM related component. Furthermore, PON also described a majority of the IncN60 variability.

Soil organic matter is the main contributor of N in soils and under the right conditions, mineralization of SOM can lead to an accrual of 80% of N supply in crops (Bu et al. 2017; Clivot et al. 2017). Particulate organic matter comprises a significant proportion of SOM, with previously reported ranges of POC as a proportion of soil organic C (SOC) of up to 40% or more. In our dataset, POC as a proportion of SOC ranged from 8.5% to 37.6%. POM has been found to have a strong influence on potential N_{min} and soil N availability (Bu et al. 2015; Martínez, Galatini, & Duval 2018; Scharenbroch & Lloyd, 2006).

Particulate organic matter is a quantitatively defined pool of SOM measured via dispersion and sieving and separated from the bulk soil along with the sand fraction (> 53 μm). Bu et al. (2015) considered the POM fraction at least partially composed of easily accessible N and very responsive to alterations in management due to its unprotected nature. This same study verified the importance of PON to potential N_{min} by incubating soils with and without their POM fraction and measuring soil mineral N content. After incubation, soils without POM mineralized significantly less N than those with POM, resulting in a reduction of potentially mineralizable N of 41.8% (Bu et al. 2015).

Particulate organic N describing a large proportion of the variability in the Core N and IncN60 N_{min} in our study is similar to findings by Bu et al. (2015), whose study resulted in an R^2

of 0.33 between potentially mineralizable N and PON. Martínez, Galatini, and Duval (2018) found that potential N_{min} was mostly determined by the various fractions within POM. Kader et al. (2010) found in their study that PON was an important predictor of the rate constant in their undisturbed and disturbed N_{min} prediction models and found a significant positive correlation between PON and N_{min} (Kader et al. 2010). However, Clivot et al. (2017) found that while soil organic N (SON) significantly improved their potential N_{min} model, PON did not improve their predictions despite PON also having strong correlations with potential N_{min} and they suspected this was due to its association with SON.

Particulate organic N is organic N not associated with clay minerals. It is considered unprotected and is thus more prone to degradation from disturbance and being mineralized by microbes. While it generally is considered a more labile fraction of SOM, its lability is somewhat debated and there have been some conflicting findings concerning its availability among other scientists (Bu et al. 2015). While the studies above agreed it was a labile fraction, some studies have found it to be more recalcitrant, and others have reported both source and sink characteristics on the POM fraction in terms of its effect on N turnover (Bu et al. 2015; Cambardella & Elliot, 1992, Franzluebbers & Arshad, 1997; Kader et al. 2010). Bu et al. (2015) found in their incubation study of rapeseed-rice (RR) rotation and cotton-rice (CR) rotation in a rice-paddy system that after spectral analysis, the RR treatment POM fraction tended to accumulate more humified and recalcitrant materials such as lignin and tannins, which resulted in less available N. Conversely, the CR treatment's POM fraction accumulated lower C:N ratio materials such as polysaccharides and carbohydrates which degrade more easily. Several other studies have also found that POM quality determines its decomposition and effect on N_{min} (Kader et al. 2010; Martínez, Galatini, & Duval 2018). Thus, the quality of the POM is likely a critical

factor in determining its accessibility to microbial degradation and ability to supply mineral N and may explain some of the contradictions found concerning POM's availability.

Silt

Silt as a textural component is considered part of the fine earth fraction and is typically associated with loess and alluvial deposition, the latter being the main pathway for soil formation in the Central Valley (Page 1986). As part of the fine earth fraction, any SOM fraction associated with silt content is considered more protected than that associated with sand, such as POM (Bu et al. 2010). However, disturbance may alter any physical protection that silt-associated SOM may have. Furthermore, silt fractions have also been found to contain significant sources of available SOM such as microbial biomass and root exudates (Kader et al. 2010). Kader et al. (2010) found that silt-N and its C:N ratio was strongly correlated with N_{min} and was included in their best fit N_{min} prediction model. Martínez, Galatini, and Duval (2018) found positive correlations between potentially mineralizable N and silt content. Miller et al. (2018) also included silt in their best fit model for predicting N_{min} in low SOM soils.

The Effect of Disturbance on N Mineralization Over Time

Previous research has indicated that disturbance (i.e. tillage) should lead to increased N_{min} (Cabrera & Kissel, 1988; Sparling and Ross, 1988). However, our N_{min} results show that only small differences were observed between sieved and undisturbed soil N_{min} (Figure 3.7). Disturbance and sieving results in mixing, oxygenation, and destruction of soil aggregates, which increases decomposition of SOM and generally enhances nutrient cycling (Cabrera & Kissel, 1988). However, due to the insignificant differences between Core N and IncN60, we rejected

our hypothesis (2) that variations in handling techniques would result in significantly different N_{min} trends between the disturbed and undisturbed samples. One explanation for this observed contradiction to prior findings could be the difference between methods utilized in previous studies and our study. Earlier researchers typically air-dried the soils prior to incubating them, which was not the case in our study where samples were incubated field moist. When soils are re-wetted after air-drying, they tend to have a large initial flush of N_{min}. Sparling and Ross (1988) concluded this post air-dry N_{min} flush likely results from decomposition of desiccated microbial necromass of low C:N ratio, which is rapidly processed upon rewetting of soil. Therefore, air-drying results in an overestimation of N_{min} upon rewetting, making predictions of potential N_{min} inaccurate (Cabrera & Kissel 1988).

The Role of Soil Moisture in Seasonal N Mineralization Over Time

Our finding that N_{min} decreases with decreasing soil moisture content, confirms our hypothesis (3) and supports previous research stating that soil moisture content is a driver of biological activity in soils, especially in N turnover (De Neve & Hoffman, 2002). Our dataset highlights how variable N_{min} is in the field under varying soil moisture conditions (Figure 3.9). This dataset further demonstrates that even at the lowest soil moisture measured, N_{min} still continued, though much slower than at 60% WHC. This result is confirmed by other studies who also found that N_{min} was greatly diminished, though still considerable, at lower soil moisture content (Cassman and Munns, 1980; Myers, Campbell, & Weier, 1981).

Considering California's historic drought conditions, many growers are converting their irrigation systems to more water-efficient methods (National Integrated Drought Information System 2021; Water Education Foundation 2021). Our research demonstrates when growers

switch to more water-efficient methods, that even relatively dry parts of the soil are continuing to supply N to the crop.

Impact of Previous Crops on Pre-plant Undisturbed Core N Mineralization

It has been suggested in earlier studies that the previous crops residue's incorporated into a field may significantly affect N_{min} (Miller et al. 2018, Wade et al. 2018). Clivot et al. (2017) found that in their best N_{min} prediction model which included cropping history explained 19% more variance than their original model. They determined that this was due to the long-term effects of added SOM and its effect on microbial biomass and N turnover. Despite these previous findings (Carpenter-Boggs et al. 2000; Clivot et al. 2017; Kaur, Cihacek, & Chatterjee, 2018; Miller et al. 2018; Wade et al. 2018), the results presented here indicate that within this dataset, the type of residues does not play a strong role. These results have been confirmed in previous work. Kaur, Cihacek, and Chatterjee (2018) found no correlation to N_{min} and residue composition at any of their experimental sites utilizing three residues: corn (*Zea mays* L.), spring wheat (*Triticum durum* Desf.), and soybean (*Glycine max*) in their 8-week incubation study. They theorized that this was due to the fact that most of the nutrients were removed with the crop during harvest. Coleman and Schimel (2013) found that the rate of N_{min} did not vary by vegetation type despite large differences in vegetation N concentration in their incubation study with 84 different soil types and four different vegetation types (grassland, shrubland, coniferous forest, and deciduous forest). In our study, the variation in crop type from the previous season likely explains the lack of effects, especially when considering that some previous crop types had multiple occurrences (i.e. processing tomatoes) while others only had one (i.e. barley). The

variation in experimental designs and statistical analysis across studies may also explain why there are mixed conclusions regarding the effect of previous crops on N_{min}.

Due to our limited data availability with each crop type, it is recommended that in future research, more sites of each crop type are included to investigate this hypothesis.

The Effect of Roots on Seasonal N Mineralization

The presence of a fully developed root system increases organic acid concentrations in the surrounding soil via exudates, adds plant biomass, provides actively decaying detritus, and is expected to impact N_{min} due to the stimulation of the microbial communities in the rhizosphere. Zhu et al. (2014) found that the presence of living root systems resulted in altered decomposition rates, increased N_{min}, microbial biomass and enzymatic activity compared to the surrounding soil. They attribute these modifications to a rhizospheric priming effect (RPE). The RPE is defined as the effect that live roots and their rhizospheric communities have on the degradation rate of SOM (Cheng et al. 2014).

The lack of any clear trends found in our data allowed us to reject our hypothesis (4) that there would be significant differences in N_{min} due to the presence of fully established roots. Fornara, Tilman, and Hobbie (2008) found in their root study that SOM decomposition and N_{min} trends differed under the legume and forb treatments when compared to grasses. With leguminous treatments resulting in increased N_{min} rates compared to the grass treatments and the control. The same subtleties may exist across the crops grown at our field sites. The fact that we did not specifically sample from the rhizosphere may explain the lack of effects. Further, we only assessed canopy coverage every 5-6 weeks at the same time as soil sampling, when it is very likely that full canopy coverage was achieved sometime within those 5-6 weeks. Thus, our

results may not reflect the true date of full-canopy coverage and thus a fully developed root system.

Regional Model Validation

When evaluating the differences in soil properties included in the models between the two studies, there were only small differences that hardly explained the poor fit for both models when testing the combined dataset (Table 3.6).

The improved R^2 of Equation 2 when compared to Equation 1 is not surprising, as it was a larger dataset. The Miller et al. (2018) dataset and our dataset comprised 68% and 32% of the combined dataset, respectively. Equation 1 and it's lower R^2 allowed us to reject our hypothesis (5) that this research would lead to an improved N_{min} prediction model for low SOM soils in the Central Valley. However, the difference is quite small, and it is recommended that further research is conducted on this topic.

Regional N Mineralization Variability: The Challenges of Predicting Seasonal N_{min}

Throughout the growing season, N_{min} varied considerably within and between sites, regardless of the soil moisture treatment. In most cases, there was no general observable pattern in increasing or decreasing N_{min} throughout the season, not even for individual sites.

These results were not unexpected, as many previous studies have found a high degree of variation in their observed N_{min} patterns (Cabrera, Kissel, & Vigil, 2005; Carpenter-Boggs et al. 2000; Clivot et al. 2017; Coleman & Schimel, 2013; Gillis & Price, 2016). Cabrera, Kissel, and Vigil (2005) attributed the high degree of observed N_{min} variability in their review to adsorption of N to clay surfaces, fluctuating levels of aeration depending on soil texture, shifting C:N ratios

of microbiota and SOM, and differences in the amount of water held at field capacity. Coleman and Schimel (2013) found that only 33% of their observed N_{min} trends could be explained with their best-fit variables: mean annual precipitation, soil C and N content, and texture (specifically clay).

While it has been established that environmental factors like precipitation and temperature drive N cycling, they often make interpreting results difficult as they usually covary with other variables and heavily impact the primary processes being studied, such as the effect that precipitation has on SOM content, leaching, and microbial communities (Coleman & Schimel, 2013). Considering that most N transformation processes likely have distinct controlling variables, many of which compete with each other (i.e., competition between microbes and clay sorption of SOM), attempts at predicting N_{min} even in a relatively small region like the Central Valley, remains a challenge. Coleman and Schimel (2013) describe this as attempting to detect "a small amount of noise on a very large signal" and perhaps once we can better understand the larger driving forces that control N_{min}, then we can better learn to detect the process in which we are invested.

3.5 Conclusion

Predicting N_{min} in the Central Valley will provide local producers with valuable information regarding fertilizer management. In this study, we found that across 17 soils from fields with annual crops, pre-plant undisturbed N_{min} could best be explained by PON and silt content. While the seasonal disturbed N_{min} was best described with PON alone. Soil moisture is a driver of N_{min}; in this study we found that even in the driest soils, N_{min} continued though at a slower rate than at optimum soil moisture. While the presence of roots and the previous year's

crop did not affect N_{min} as expected, it is still recommended that further research is pursued in regard to both of these potential sources of seasonal N_{min} variation. The high level of variability in N_{min} across the region highlights the challenges that still exist for researchers and producers alike.

4. How Incorporating Seven Annual Crop Residues Alters N Turnover

4.1 Introduction

The carbon:nitrogen (C:N) ratio is an important factor affecting N mineralization (N_{min}) from organic materials, including crop residues. This is due to the stoichiometric relationship between C and N metabolic requirements of saprophytic microbes and the C and N supplied by organic substrates (Bonanomi 2019). It is generally assumed that the defining cutoff for N_{min} lies approximately at a C:N ratio of 20:1 (Havlin et al. 2016). With greater C:N ratios in the substrate, soil microbes require more N for growth and metabolism than is available in the substrate and thus immobilize N from soil solution (Bonanomi 2019, Havlin et al. 2016). In contrast, with a C:N ratio below 20:1 in the substrate, N is available in excess of microbial demand, resulting in the release of ammonium into soil solution (Havlin et al. 2016). However, the C:N ratio has proven to be insufficient in its ability to accurately determine whether certain residues mineralize or immobilize N. Bonanomi (2019) theorize that this insufficiency could be due, in part, to the lack of information about the quality and composition of the C. Berg and McClaugherty (2008) concluded that because the C:N ratio of a residue changes as decomposition proceeds, it is not recommended for use in efforts to estimate residue decay rates.

Berg and Matzner (1997) discussed a multi-phase approach to estimating decay rates. They described how the C:N ratio along with accessible nutrients are dominant in determining the rate of decay during early stages of decomposition. Then, as those easily accessible compounds decrease and more recalcitrant materials accumulate, that lignin content is a better predictor of decay rates during the later stages of decomposition. Lignin, as well as the lignin:N ratio, is especially important in systems where the residues have a high lignin content, whereas in

systems with residues low in lignin, the C:N ratio may play a more important role (Bonanomi et al. 2013). Lignin has been shown to physically and chemically shield soil organic matter (SOM) and specifically N-compounds from microbial consumption, potentially through the formation of cross-linkages with accessible compounds that prevent decomposition (Talbot et al. 2012; Walela et al. 2014).

The objective of this study was to determine the effect of different fall-incorporated crop residues with different C:N ratios on soil mineral N content during the winter and on N_{min} in the spring. We hypothesize that there will be differences observed in N turnover among the residues incorporated as well as when compared to the control (no residue treatment).

4.2 Materials and Methods

Crop residue samples were collected from grower's fields just prior to harvest in the fall of 2019. Seven residues were collected, namely corn (*Zea mays*), watermelon (*Citrullus lanatas*), safflower (*Carthamus tinctorius*), sunflower (*Helianthus annuus*), sorghum (*Sorghum bicolor*), processing tomatoes (*Solanum lycopersicum*), and cotton (*Gossypium hirsutum*). Residues were collected from four replicated areas of 2.2 m^2 in each field. Plants were cut at the base, the harvested organs were removed and packed into bags. The residues were then air-dried on a tarpaulin outside. Once thoroughly dried, the residues were coarsely chopped utilizing a garden shredder/chopper (Sears Craftsman) with a collection bag attachment and then stored in large plastic bags in a covered area. Subsamples were brought back to the lab where they were ground into a fine powder and analyzed for total C and N using dry combustion analysis with a Costech Elemental Combustion System (ECS 4010). Furthermore, samples were sent to the UC Davis Analytical Lab to determine lignin, cellulose, and hemi-cellulose contents, using the reflux

methods for the determination of acid detergent fiber and neutral detergent fiber based on Goering and Van Soest (1970) (Table 4.1).

A field trial was conducted at UC Davis' Campbell Tract Facility in a field which was fallow during the previous growing season. The soil at the site was a Yolo silt loam, classified as a fine-silty, mixed, superactive, nonacid, thermic Mollic Xerofluvents, on 0-2% slopes formed on alluvial flood plains (Custom Soil Resource Report, 2019). On October 25th, 2019, each of the seven residues was applied to four replicate plots in a completely randomized block design, including a control plot in each block. Each plot was approximately 1.8 m wide and 1.5 meters long, including 0.3-m wide walking aisles surrounding each plot. The amount applied per unit area of each residue corresponded to the amount removed from the grower's fields. Residues were tilled into the surface soil to a depth of 15 cm with a rototiller.

Soil samples were collected prior to field trial initiation. Four samples were taken using an auger or soil probe from each block for a composite sample. Separate samples were taken from the 0-30 cm and 30-60 cm layers and kept cool in an ice chest. Between December 2019, after the winter's rain started, until just prior to the spring planting date in April 2020, soil samples were taken every 4-6 weeks. At the final sampling date on April 14th of 2020, undisturbed soil cores (15 cm long and 5 cm diameter) were taken from each plot along with the regular soil samples. Prior to core sampling, the top 2-3 cm of soil consisting of dry crust was removed. Together with the undisturbed cores, a separate soil subsample was taken from the same layer with a probe from the area surrounding each core.

Once samples were brought back to the lab, they were sieved to 4 mm and analyzed for gravimetric soil moisture by drying a subsample at 105 °C for 24 hours and mineral N using potassium sulfate (K_2SO_4) extractions and colorimetric analysis of ammonium-N (NH_4^+-N) and

nitrate-N (NO_3^--N). In addition, soils were analyzed for total C and N, texture, microbial biomass C (MBC), particulate organic matter C and N (POM), electrical conductivity (EC), and pH. A summary of the soil analysis results is shown below in Table 4.2. A full description of the methods can be found in the Materials and Methods section of the main study (Chapter 3).

Soil samples collected every 5-6 weeks during the winter and early spring were analyzed as mentioned above for gravimetric soil moisture and mineral N (sum of NH_4^+-N and NO_3^--N).

The subsamples collected from the surrounding soil of the undisturbed core samples in spring was used to determine initial mineral N and gravimetric soil moisture content in each core. Back in the laboratory, the soil cores were adjusted to 60% water holding capacity (WHC) with deionized (DI) water using a syringe and side-port needle and placed in an incubator at 25 °C for 10 weeks. Soil moisture was maintained throughout the incubation via weekly applications of DI water with a pipette to the soil surface. At the end of the incubation, the cores were sieved to 4 mm and analyzed for mineral N.

Table 4.1. Seven residue's characteristics and application rates. Residues were analyzed for total C, total N, C:N ratio, lignin, cellulose, and hemi-cellulose. Standard deviations are shown below the means in parentheses.

Residue	C (%)	N (%)	C:N	Application Rate (t/ha)	Lignin (Ash-Free) (%)	Cellulose (%)	Hemi-Cellulose (%)
Corn	43.4 (0.2)	0.9 (0.04)	46.0 (2.3)	4.0	3.5	32.3	33.8
Cotton	42.8 (1.0)	1.3 (0.3)	33.9 (6.6)	8.6	7.1	41.0	12.9
Melon	40.4 (1.0)	1.4 (0.03)	29.9 (0.9)	2.8	4.6	23.3	10.5
Safflower	40.7 (3.9)	0.9 (0.1)	46.6 (2.2)	2.1	5.5	33.9	19.7
Sorghum	40.4	0.3	140.5	5.9	3.9	29.4	28.0

	(0.1)	(0.01)	(3.9)				
Sunflower	40.8 (0.1)	0.9 (0.02)	45.9 (0.9)	2.3	6.3	32.4	14.2
Tomato	28.7 (0.5)	0.9 (0.03)	19.2 (0.2)	8.1	4.4	24.9	12.1

Table 4.2. Characteristics of the soil at the trial site. All values are from soils sampled to 30 cm depth.

Property	Measurement	Standard Deviation
Sand (%)	24.0	0.7
Silt (%)	47.1	0.8
Clay (%)	28.9	0.1
pH	7.7	0.1
EC (μS cm^{-1})	150.5	86.2
Total C (%)	0.91	0.03
Total N (%)	0.10	0.01
C:N	9.3	0.2
POC (% of total C)	10.2	5.0
PON (% of total N)	9.9	3.8
MBC (mg C kg^{-1} OD soil)	14.6	10.2
Mineral N (mg kg^{-1})	14.6	9.9

Daily soil temperature at a depth of 15 cm and precipitation data were gathered from the California Irrigation Management Information System (CIMIS) for the duration of the field trial (Figure 4.1, CIMIS 2020). The weather station was located in an adjacent field.

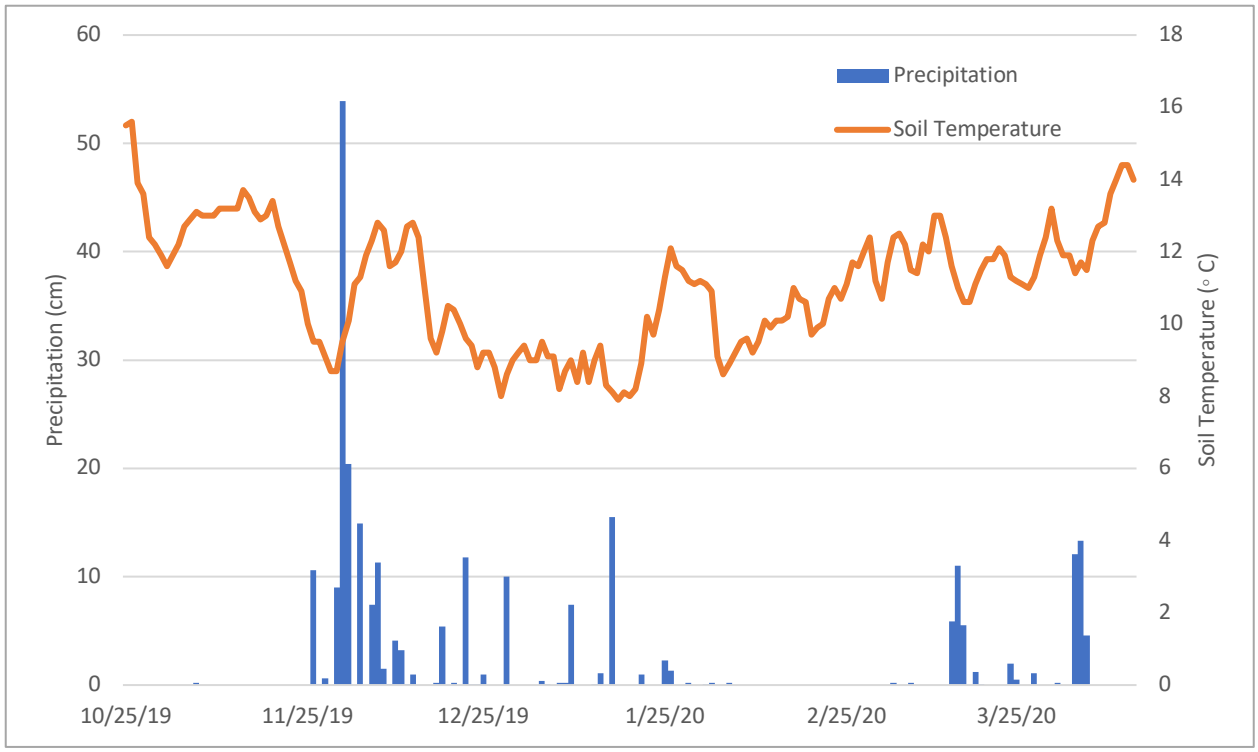


Figure 4.1. Daily precipitation and average soil temperature data at the field site. Data was collected from the California Irrigation Management Information System (CIMIS) for the duration of the field trial (CIMIS 2020).

Statistical analyses were performed on the data from each sampling date as well as on the soil core data. The dependent variable of soil mineral N was log-transformed to correct for heteroscedasticity. A linear model in R-Studio (v. 1.3.1093) using the lm() function was utilized. When a significant effect was found on the linear model using ANOVA, this was followed by means comparisons with both a control vs. treatment Dunnett Method comparisons, as well as a Tukey test pairwise comparison to assess differences across all treatments. Effects were considered significant for $P < 0.05$. It is noted that there was a strong blocking effect, and this accounted for a majority of the variation within the dataset and was adjusted for in the analysis by including it as a random factor to account for its large contribution to the overall variability.

4.3 Results

The Effect of Crop Residues on Winter N Mineralization Under Field Conditions

Between the trial initiation and the first sampling date on December 17th, 2019, there had been 138.9 mm of rainfall, the majority of which fell at the beginning of December (Figure 4.1). Average gravimetric soil moisture in the top 0-60 cm was 0.18 g H_2O g^{-1} oven dry (OD) soil (40.7% WHC, Figure 4.2). Mineral N in the residue treatments was lower in all treatments than in the unamended control, suggesting that the residue additions initially immobilized N, with sorghum immobilizing the most, and cotton along with tomato immobilizing the least, though none of the treatments were significantly different from the control (Figure 4.3 and Table 4.3).

At the second sampling date on January 26th, 2020, there had been an additional 58.2 mm of precipitation since the last sampling (Figure 4.1), and average gravimetric soil moisture in the top 0-60 cm was 0.23 g H_2O g^{-1} OD soil (52.3% WHC, Figure 4.2). All residue treatments with the exception of safflower, were beginning to mineralize N when compared to the first sampling date, though mineral N in residue-amended plots remained lower than in the control. Sorghum maintained the highest degree of immobilization in comparison to all other treatments. None of the treatments significantly varied from the control (Figure 4.3 and Table 4.3).

At the third sampling date on March 13th, 2020, there had been only an additional 1.1 mm of precipitation since the last sampling date (Figure 4.1). Average gravimetric soil moisture in the top 0-60 cm was at 0.18 g H_2O g^{-1} OD soil (40.7% WHC, Figure 4.2). All residue treatments (with the exception of sunflower) had been mineralizing N since the previous sampling date (Figure 4.3). However, with the exception of tomato and cotton, the mineral N content in the residue-amended soil was still lower than in the control. At this point in time, sunflower and

sorghum residues had the lowest mineral N content, while cotton had the highest. None of the treatments significantly differed from the control (Figure 4.3 and Table 4.3).

By the final sampling date on April 14th, 2020, there had been an additional 57.5 mm of rainfall since the last sampling (Figure 4.1). Average gravimetric soil moisture in the top 0-60 cm was 0.20 g H_2O g^{-1} OD soil (45.1% WHC, Figure 4.2). The soil mineral N content was still higher in the control than in all treatments with the exception of tomato and cotton. Net N_{min} took place in all residue treatments except for melon, sunflower, and corn. The mineral N content continued to be highest in the cotton treatment and lowest in the sorghum treatment. A Tukey Test indicated a significant difference between cotton and sorghum at the 0-30 cm sampling depth (P = 0.0204). The difference in mineral N content between these two residue treatments was 14.3 mg N kg^{-1} OD soil, corresponding to approximately 59.4 kg N ha^{-1} in the top 30 cm of the soil profile. None of the treatments significantly varied from the control (Figure 4.3 and Table 4.3).

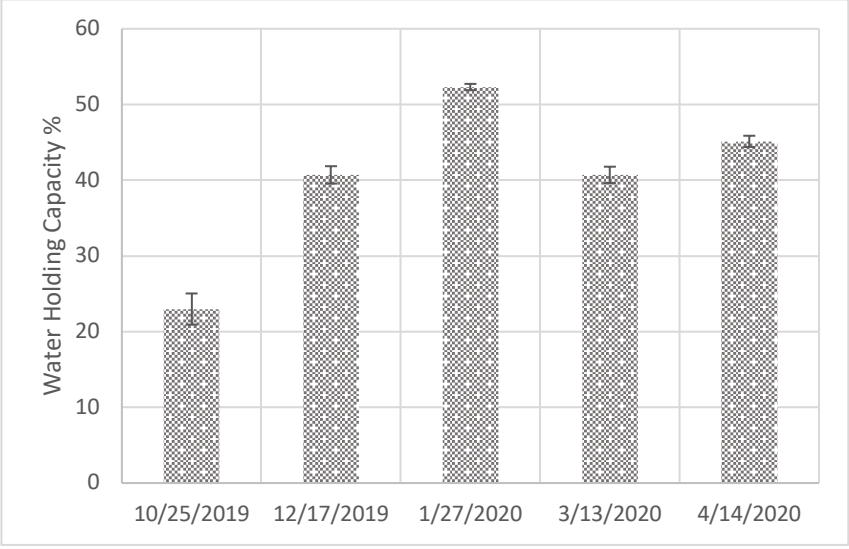


Figure 4.2. Average soil moisture at 0-60 cm at each sampling date is shown as percent water holding capacity. Error bars represent standard error.

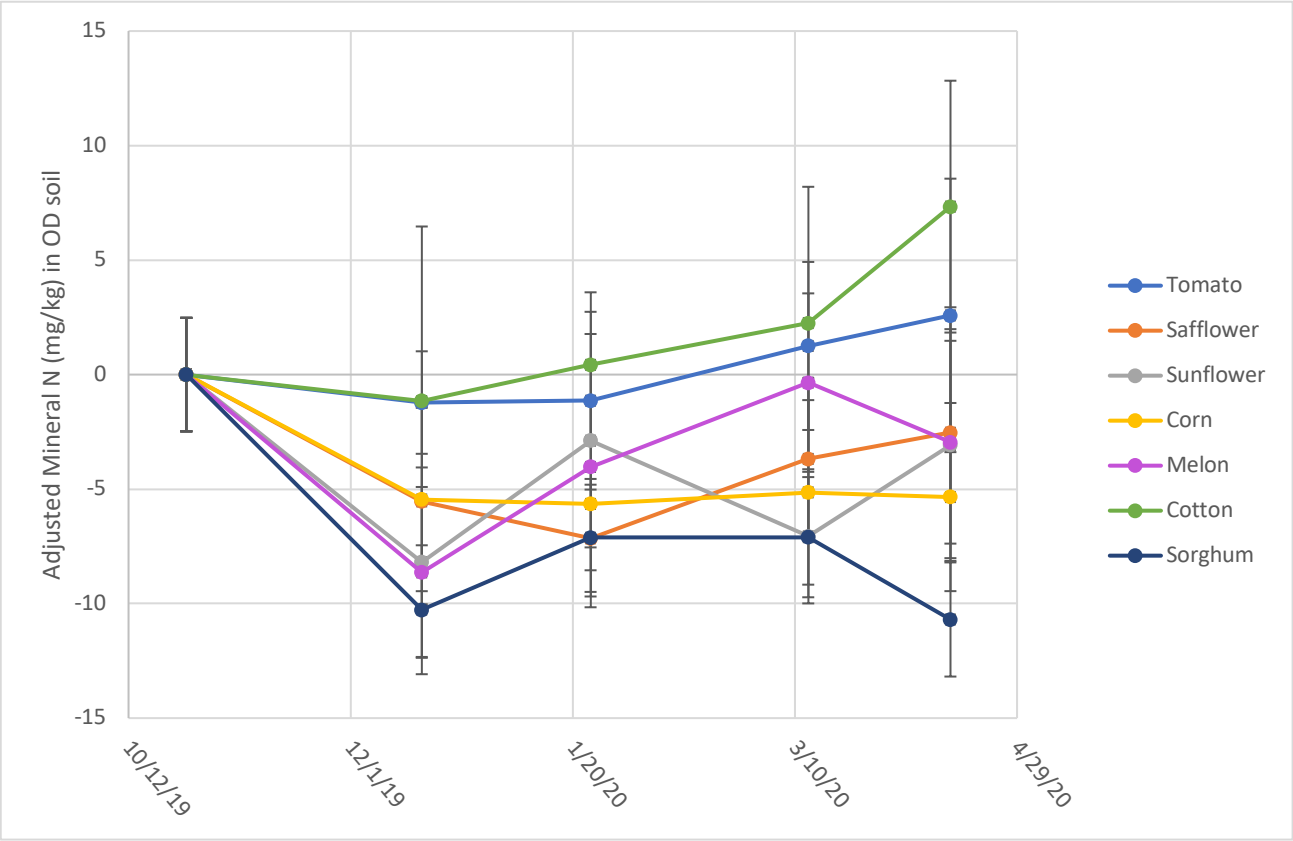


Figure 4.3: Changes in mineral N in the soil profile (0-60 cm). Shown are the differences in soil mineral N (sum of ammonium-N and nitrate-N) content between the residue-amended treatments and the unamended control (y = 0; adjusted mineral N) at four sampling dates throughout the winter of 2019 and spring of 2020. Error bars represent standard error.

Table 4.3: Total mineral N (mg mineral N kg^{-1} OD soil) measured at each sampling date for both 0-30 cm and 30-60 cm sampling depths. Superscript a or b indicate significant differences ($P < 0.05$) across residue treatments at the same sampling date.

	0-30 cm							
Date	Tomato	Safflower	Sunflower	Corn	Melon	Cotton	Sorghum	Control
10/25/19	14.64	14.64	14.64	14.64	14.64	14.64	14.64	14.64
12/17/19	9.89	8.64	7.62	10.21	7.40	11.36	6.35	13.22
1/24/20	11.27	7.43	9.42	8.45	8.45	12.44	7.65	11.56
3/13/20	9.52	7.79	4.79	8.06	8.06	11.46	5.68	9.89

4/14/20	17.66 [ab]	12.83 [ab]	13.91 [ab]	12.84[ab]	14.82[ab]	22.92[a]	8.59[b]	14.96[ab]
30-60 cm								
10/25/19	11.05	11.05	11.05	11.05	11.05	11.05	11.05	11.05
12/17/19	13.93	10.87	9.23	9.38	9.01	12.53	8.43	11.83
1/24/20	10.77	8.59	10.86	9.07	9.38	11.16	8.40	11.61
3/13/20	11.18	7.98	7.60	6.25	9.55	10.24	5.68	9.56
4/14/20	9.76	9.47	7.85	6.65	7.07	9.25	5.55	9.88

Undisturbed Core Incubations

During the 10-week incubation of undisturbed soil cores, net N_{min} was highest in the cotton residue treatment and the lowest in the sunflower treatment (Figure 4.4). The difference between the two treatments was 13.7 mg N kg^{-1} OD soil, or approximately 28.4 kg N ha^{-1} in the top 15 cm of the soil. All treatments had mineralized more than the control except for the sunflower and safflower treatments (Figure 4.4). However, these effects were not statistically different. Among the residue treatments, only the sunflower and cotton residue treatments differed significantly from each other ($P = 0.0447$). There was a weak difference between tomato and sunflower as well ($P = 0.0901$, Figure 4.4).

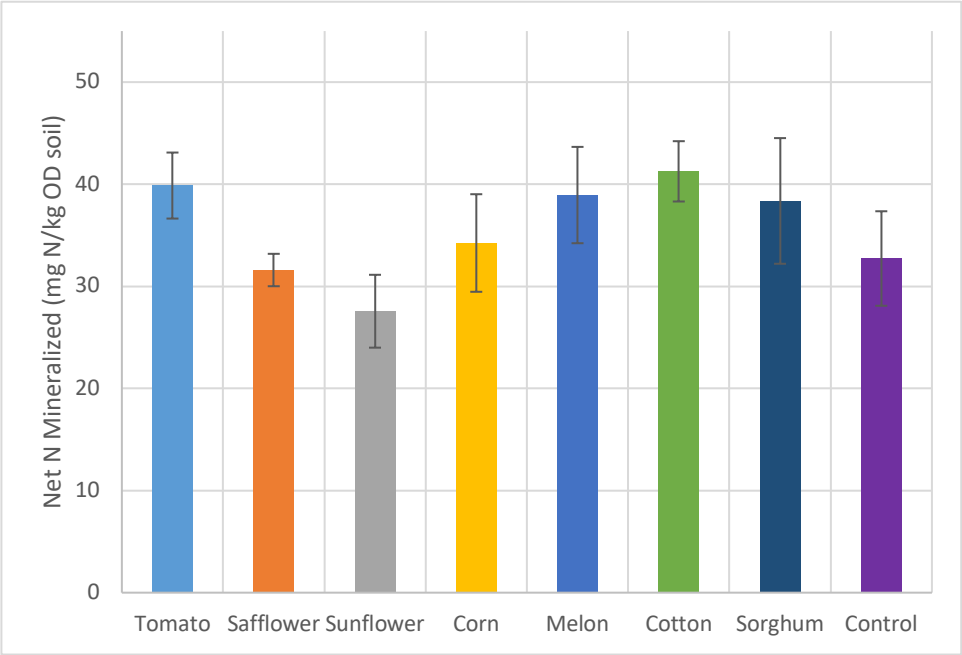


Figure 4.4. Net N mineralization during a 10-week incubation of undisturbed soil cores at 25° C and 60% water holding capacity utilizing seven residue treatments. Cores were collected from the top 15 cm of soil profile. Error bars represent standard error.

Expressing the results of both the field trial and the undisturbed core incubation per unit of residue N incorporated showed that cotton mineralized the most N, while sorghum immobilized the most N during the field trial. However, during the undisturbed core incubation the sunflower residue immobilized the most N (Figures 4.3 and 4.5). From these results, three distinct net N immobilization-mineralization patterns can be distinguished. The first group will be referred to as the "slow" mineralization group and includes safflower and sunflower. These two residues led to net N immobilization during the winter as well as during the core incubation, meaning that the mineral N content in the soil amended with these residues never exceeded the mineral N content in the control. These two residues are characterized by a similar C:N ratio of approximately 46:1, the same total N of 0.9%, and similar total C of 41% (Table 4.1). These two

residues also share roughly similar lignin, cellulose, and hemi-cellulose concentrations of 5.5% and 6.3%, 33.9% and 32.4%, as well as 19.7% and 14.2% for safflower and sunflower, respectively (Table 4.1). Furthermore, they shared the lowest application rates of 2.1 t ha^{-1} and 2.3 t ha^{-1} for safflower and sunflower, respectively (Table 4.1).

The second group will be referred to as the "medium" mineralization group and includes corn, melon, and sorghum. These residues led to net N immobilization in the field trial, but net N_{min} during the undisturbed core incubation (Figures 4.3 and 4.5). Large differences were observed in C:N ratio which ranged from 30:1 to 141:1 (melon and sorghum, respectively) (Table 4.1). For the lignin, cellulose and hemi-cellulose content, the variation across hemi-cellulose was greatest, ranging from 11% to 33.8%, while lignin and cellulose content ranged from 3.5% to 4.6% and 23% and 32%, respectively (Table 4.1). The application rates ranged from 2.8 t ha^{-1} to 5.9 t ha^{-1} (melon and sorghum, respectively; Table 4.1).

Finally, the third group will be referred to as the "fast" mineralization group and includes the tomato and cotton residue treatments which mineralized more N than the control during the field trial and continued to do so for the remainder of the experiment (Figures 4.3 and 4.5). These residues are characterized by a C:N ratio of 34:1 and 19:1, for cotton and tomato, respectively (Table 4.2). They also differed in their lignin, cellulose, and hemi-cellulose contents of 7.1% and 4.4%, 41% and 24.9%, as well as 12.9% and 12.1% for cotton and tomato, respectively. Application rates were 8.6 t ha^{-1} and 8.1 t ha^{-1} for cotton and tomato, respectively (Table 4.1).

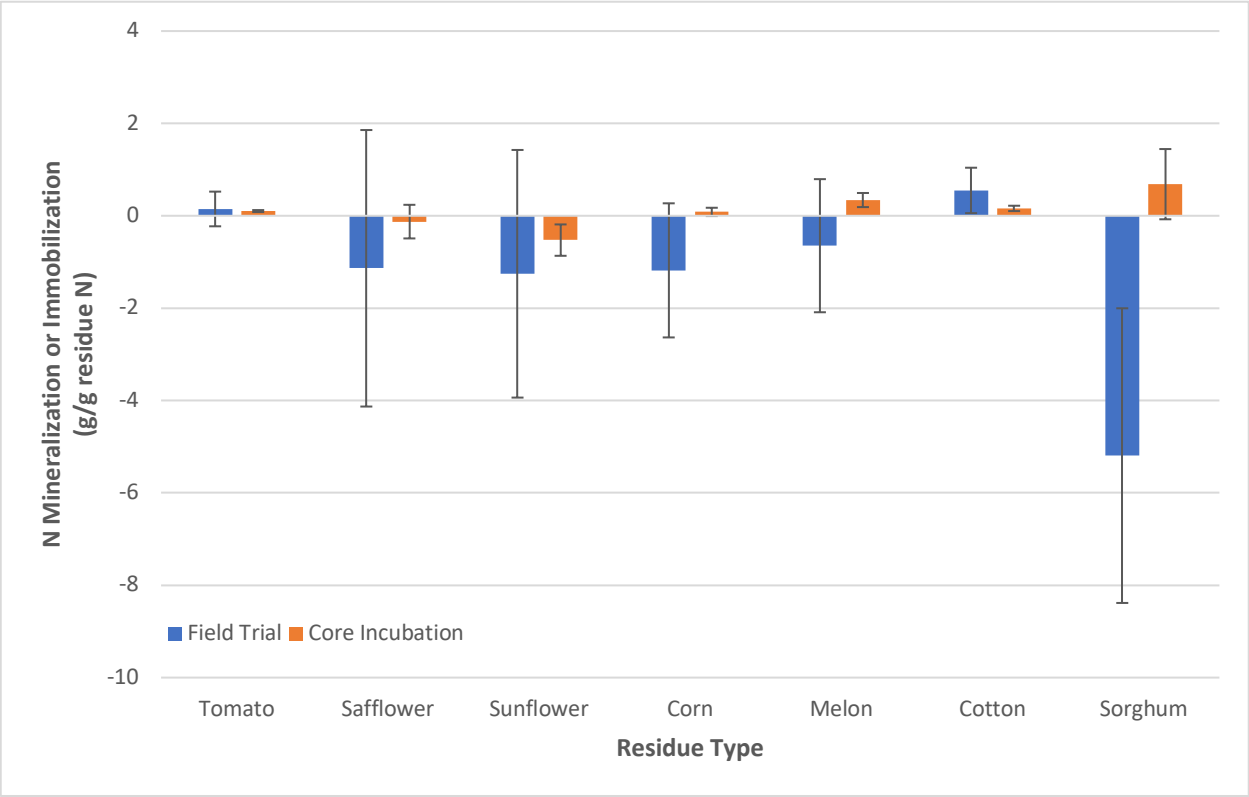


Figure 4.5: Net N immobilization or mineralization (expressed as g N mineralized or immobilized g^{-1} applied residue N) for the final field trial sampling date. Final sampling date was in April 2020 (blue bars) and the following 10-week undisturbed core incubation maintained at 60% water holding capacity and 25 °C (orange bars) harvested in June 2020. Field trial data shows the differences in mineral N between the control and the residue treatments in the top 60 cm of the soil profile. The undisturbed cores were taken from the top 15 cm of the soil profile. Error bars represent standard error.

4.4 Discussion

Mineralization and immobilization of N are happening simultaneously in any soil. This study illustrates the complexity of the mineralization-immobilization continuum across multiple types of incorporated residues starting from incorporation until the peak of the following growing season. Nitrogen turnover in the field trial represents initial decomposition during the fallow overwintering season after residue incorporation, while the N turnover that took place during the incubation is the potential effect of fall-incorporated residues on N_{min} during the following growing season. The undisturbed soil cores were taken around the same time that seeding usually takes place in grower's fields in the spring. The cores were incubated at 25 °C and 60% WHC representing soil temperature and moisture during summer months under irrigation. For comparison, weather data collected from the CIMIS station in an adjacent field during August of 2020 show that average soil temperature was 22.9 °C and reached a peak of 24.8 °C in mid-August (CIMIS 2020). A laboratory incubation is a valuable approach to compare different residue types, but the N_{min} rates may differ from those in the field. An undisturbed soil core incubation does not take into account how tillage aerates the soil and would likely result in an increased decomposition rate. Nor does it take into account the wetting and drying cycles that occur in a field setting. Previous research has shown that residue decomposition rates are lower when subjected to wetting and drying cycles than when continuously moist (Cabrera et al. 2005).

Comparisons Across Crop Residue Groups: Slow, Medium, and Fast N_{min}

Cotton mineralized the most N throughout the experiment, indicating that this residue's properties allow for rapid decomposition by microbes when compared to the other residue

treatments. Despite it having the greatest application rate at 8.6 T ha^{-1}, its relatively low C:N ratio (34:1), low lignin:N ratio (5.5), and overall compositional quality allowed microbes' easy access to its organic N compounds (Figures 3, 4 and 5). A study by Walela et al. (2014) found that despite having a high C:N ratio of 94.4, oat (*Avena sativa*) residue was of a very high quality, meaning the residue had higher concentrations of accessible C compared to the other residues utilized, leading to that residue's rapid microbial consumption. The cotton residue exhibited N_{min} rates that indicate its rate of decomposition was higher than that of the other residues, despite a short initial period of immobilization. However, the trends we see with the cotton residue may differ somewhat from what would be observed in a commercial field. In this trial the cotton residue still had some lint and seed remaining on the stems. Therefore, the trends observed with this residue treatment may not fully represent the trends in commercial fields where the lint and seed would not be included.

In contrast, the slow group continued to strongly immobilize N until the end of the field trial, suggesting the opposite applies to this group's C availability. This could potentially be explained by a combination of factors such as the C:N ratio, lignin:N ratio or other chemical properties such as cellulose or hemi-cellulose content as well as the various functional groups that compose those structural components. For example, the C:N ratios for cotton and sunflower (34:1 and 46:1, respectively) and lignin:N ratios (5.5 and 7.1, respectively) suggest a faster decomposition rate and higher N_{min} rate for cotton compared to sunflower. Though the same rationale doesn't help explain differences observed across the fast, medium, and slow groups.

Comparisons Within Crop Residue Groups: Slow, Medium, and Fast N_{min}

Within the fast N_{min} group, both cotton and tomato residues immobilized soil N to similar degrees (Figure 4.3). However, throughout the field trial and continuing into the undisturbed core incubation, tomato residues mineralized less N than the cotton (Figure 4.3 and 4.5). This is contradictory to what would be expected, considering that cotton had higher C:N and lignin:N ratios. (Table 4.1). With the residue analysis performed in this study, this difference cannot be explained.

In the slow group, while both sunflower and safflower residues resulted in prolonged immobilization of N relative to the control, the sunflower residue immobilized N to a greater extent than the safflower residues (Figure 4.5). These two residues had similar total C and N contents and C:N ratios, as well as similar application rates and composition. The observed continued immobilization of the sunflower and safflower residues during the undisturbed core incubation coincides with other studies. Corbeels et al. (2000), observed continued net immobilization of sunflower residue N by the end of a 224-day incubation maintained at 22 °C and soil moisture content held at 80% WHC. This continued immobilization could be from slow decomposition due to a low C availability, which is supported by several other studies (Bonanomi et al. 2019, Redin et al. 2014, Rodríguez-Lizana et al. 2010). Rodríguez-Lizana et al. (2010) found that only 39% of the sunflower residue treatment had decomposed in the field by the end of the 4.5-month in-field decomposition period. This is further supported by an incubation study by Redin et al. (2014) with 25 different residue treatments, including corn, sunflower, and sorghum. They found that the sunflower residue treatment had the lowest C-mineralization rate constant resulting in the slowest decomposition rate of all the residue treatments.

Interpretation of the results within the medium group is challenging as there are no clear trends that could be explained by the residue analyses performed. Sorghum residues stand out from both the corn and melon residues in its N_{min} behavior over the duration of the experiment. Sorghum had the greatest rate of immobilization throughout the field trial. Its rapid N_{min} during the undisturbed core incubation sets it apart from both corn and melon residues that both immobilized less during the field trial and mineralized less during the undisturbed core incubation when compared to the sorghum. Sorghum had the highest application rate, the highest C:N ratio (141:1), and the lowest total N of all the residues in the trial at 0.3%. The high application rate of sorghum residue may have also made it more difficult for microbes to decompose the large volume of organic material (Table 4.1). However, while the lignin:N ratio (14:1) was highest of all the residues, the lignin content in the cell walls was relatively low, suggesting that the cell walls may have been readily degraded, increasing the demand of N by the microbial community early on. These properties of the sorghum residue may explain why it immobilized more N per unit residue in the field trail than melon and corn (Figure 4.5).

When comparing corn residue to melon residue, corn immobilized more N during the field trial than melon and mineralized less N during the undisturbed core incubation (Figure 4.5). The corn residue had a C:N ratio of 46:1, and the melon had 30:1. The application rate of the corn was approximately three-fold that of the melon. The higher C:N ratio could explain its greater degree of N immobilization during the field trial.

Both the field trial and undisturbed core incubation resulted in no significant treatment effect relative to the control. Within the residue treatments, the chemical analyses performed could not explain all of the N turnover patterns observed. Other residue compositional analysis may be necessary to reveal factors leading to the observed trends. Bonanomi et al. (2019) found

that N_{min} rates among residues often did not match the expected rates based on C:N or lignin:N ratio, or concentrations of cellulose, hemi-cellulose, or lignin. They postulated that this is because this type of broad data actually tells us very little about the residue's biochemical composition (i.e., the functional groups and bond types within the residues structural components such as lignin or cellulose). This biochemical information might be the key to our understanding of how residues affect N_{min}. It may ultimately determine how that residue is processed by microbes (Bonanomi et al. 2019). Bonanomi et al. (2013) found that the ratio of the O-alkyl-C of carbohydrates and the methoxyl-C of lignin, as determined via carbon-13 nuclear magnetic resonance (^{13}C-NMR) analysis of their residues, had the highest correlation with the decay rate of residues. As N and C cycling are tightly coupled, the decomposition and mineralization of the C compounds within the residues likely affect the N_{min} and immobilization dynamics. Further, using Carbon-13 Cross Polarization and Magic Angle Spinning Nuclear Magnetic Resonance (^{13}C-CPMAS NMR) solid state spectroscopy, Bonanomi et al. (2019) showed that the spectral regions associated with carbonyl-C of organic acids and amides, and the N-alkyl-C regions associated with proteins and polypeptides, as well as the methoxyl-C of lignin were significantly correlated with N_{min}. They found that residue analysis using ^{13}C-CPMAS NMR solid state spectroscopy allowed them to not only categorize residues according to C quality and composition and the dominant functional groups within each residue type, but the data also allowed them to explain N_{min} trends that were otherwise inexplicable by the more common analyses.

Therefore, while the C:N ratio, lignin:N ratio, and cellulose and lignin contents may provide a general idea of the N_{min} pattern of a residue type, more in-depth residue quality analyses may be needed to gain further insight into N cycling patterns.

4.5 Conclusion

All residues initially immobilized N when compared to the control, with some even up to the final field sampling date. This shows that there is potential for the mitigation of nitrate leaching during the winter and into spring, when precipitation in California is greatest and leaching of N is most likely to occur (Chen et al. 2014). Particularly sorghum holds the most promise for this type of management strategy with its ability to immobilize N strongly, with some potential for sunflower as well.

The observed continued N immobilization in the sunflower and safflower residue treatments until the end of the trial, when compared to the control, indicates that incorporation of these residues may present a higher risk of immobilizing N fertilizers (Corbeels et al. 2000). Residues similar in composition (i.e. safflower and sunflower are both members of the Asteraceae family) may have the same effect. In contrast, for crops like cotton and tomato, incorporation of these residues may lead to an accumulation of N in the soil in late winter or spring that could result in leaching with late winter rains or heavy pre-irrigation. However, the N_{min} potential of these residues is much lower than for some other vegetables, such as broccoli (see Chapter 5).

There was also the potential for N loss during the field trial. Losses of N within a soil profile can be from leaching, volatilization (from ammonia and gaseous denitrification), and plant uptake. These losses could result in an underestimation of potential N_{min} for this trial. The field used in this study was fallow during the sampling season, thus excluding plant uptake as an N loss mechanism. To capture nitrate leached from the topsoil, the soil was sampled down to 60 cm in depth (Table 4.3). Leaching below 60 cm was likely minimal, as there was a total of only 256 mm of rainfall during the winter season, with the majority during December and January,

when net N immobilization was greatest. This implies that denitrification was also minimal during the trial. Denitrification is mainly an issue under saturated soil conditions, especially in clay-rich soils when anaerobic processes dominate N cycling processes. While denitrification may have occurred in saturated microsites in the field trial or when adding water to maintain soil moisture for the undisturbed core incubations, gaseous N losses were likely minimal.

For growers across the Central Valley, understanding N dynamics in the field after residues are incorporated is critical for planning fertilizer applications for the next growing season. Our study showed that the type of reside incorporated in fall can have a strong effect on the amount of mineral N in the soil by spring planting, highlighting the need for soil analyses so that residual soil nitrate may be accounted for to reduce overapplication of N fertilizer. The residues utilized in this study are common in the Central Valley, making these results highly relevant to local producers.

5. Effects of Residue and Soil Moisture on N Mineralization, an Incubation Study

5.1 Introduction

In California, it is a common practice to incorporate crop residues after harvest in the fall. Incorporation of crop residues can reduce pest and disease pressure and recycles plant nutrients. Mediterranean climates, like in California, are characterized by mild temperatures in fall and winter, which results in continuing decomposition of crop residues. Residue decomposition rates are mainly determined by their biochemical properties such as nitrogen (N) content, carbon (C) to N ratio, soluble carbohydrates, lignin content, as well as environmental factors, such as temperature, moisture, and soil characteristics (Dirks et al. 2010; Kutlu et al. 2018; Thapa et al. 2021). The risk of nitrate (NO_3^-) leaching in fallow fields can be high during the rainy winter season when readily decomposable residues with a high N content are incorporated. One potential approach to reduce the risk of NO_3^- leaching is to allow residues to dry on the soil surface prior to incorporation. The reduction in residue moisture in conjunction with relatively dry soils at the end of the growing season likely slows the decomposition process and thus N mineralization (N_{min}). Soil moisture has been well studied in its effects on the rate of decomposition and net N_{min}. In general, increasing soil moisture results in increased decomposition rates and N_{min} until the soil moisture content approaches anaerobic conditions (Cassman & Munns, 1980; Klemedtsson, Svensson, & Rosswall, 1988; Myers, Weier, & Campbell, 1982; Quemada & Cabrera, 1997). However, the effects of residue moisture on net N_{min} have received less attention. Most studies investigating residue decomposition and the effects on N_{min} use dried and finely ground residues to improve ease of application and to reduce variability. There is also a growing body of work that utilizes chopped and rehydrated residues in

decomposition studies (Kutlu et al. 2018; Quemada & Cabrera 1997; Quemada & Cabrera 2002; Thapa et al. 2021). However, studies utilizing fresh residues are uncommon.

Incubation studies with processing tomato residues and broccoli residues were performed. The objective was to determine the effects residue moisture and soil moisture content on net N_{min} and their interaction. We hypothesized that (1) soil moisture will have a stronger effect on net N_{min} than residue moisture and that (2) the effects would be more pronounced with broccoli residues, as they have a narrower C:N ratio and higher N_{min} potential.

5.2 Material and Methods

Two separate residue incubation experiments were performed. The first was done in fall 2018 with processing tomato residues and the second in fall of 2020 with broccoli residues. In late August of 2018, just prior to the tomato harvest, residue samples were taken from an experimental field near Davis, CA. The entire tomato vines, with the exception of the large main stems, were collected. The vines were then cut up into 1-cm pieces by hand and mixed thoroughly. The residues were then divided into three parts of equal weight. One part was placed in a plastic bag and frozen immediately, the second part was partially dried at room temperature for three days and then frozen, and the third part was air-dried until reaching a constant weight. The fresh, partially dried and air-dry samples had moisture contents of 85, 65, and 7%, respectively. In spring of 2020, broccoli residues were collected in a commercial field in Salinas, CA, chopped into 1-cm pieces and mixed thoroughly. The residues were then treated as described for the tomato vines. The moisture contents for the fresh, partially dry, and air-dry were 88, 74, and 7%, respectively. Residue samples were analyzed for total C and N by dry combustion on a Costech CN analyzer. Furthermore, a subsample was sent to the UC Davis

Analytical Lab to determine lignin, cellulose, and hemi-cellulose contents using reflux methods for the determination of acid detergent fiber and neutral detergent fiber based on Goering and Van Soest (1970). The residue properties are shown in Table 5.1. Tomato residues had a wider C:N ratio, as well as greater lignin, cellulose, and hemi-cellulose contents than the broccoli residues.

Table 5.1: Properties of the tomato and broccoli residues used for the incubation study.

Residue	Lignin (%)	Cellulose (%)	Hemi-cellulose (%)	Total C (%)	Total N (%)	C: N ratio
Tomato	4.4	24.9	12.1	34.4	1.8	19:1
Broccoli	2.9	21.7	9.4	38.0	3.6	11:1

Soil samples were collected from a field near Davis, CA for both residue incubations. The soil was classified as a Yolo silt loam on 0-2% slopes formed on alluvial flood plains (Custom Soil Resource Report, 2019). Soils were collected from the top 15 cm of the profile prior to starting the incubations, sieved directly in the field to 8 mm, thoroughly mixed and filled into 5-gallon buckets. Samples were collected from four plots which served as replicates for the incubation study. The soil samples were air-dried at room temperature (23 ºC) in a thin layer and stored in a cold room at 4 °C until incubation initiation. Subsamples were sieved to 2 mm, finely ground, and analyzed for total C and N via dry combustion (as described previously in Main Study Materials and Methods). The total C and N for the soil were 0.91% and 0.10%, respectively. Soil pH and electrical conductivity (EC) were measured using a 2:1 deionized (DI) water and soil suspension, resulting in a pH of 7.6, and EC of 0.22 mS cm^{-1}.

Each incubation was set up as a two-way factorial, completely randomized block design. The two factors were soil moisture and residue moisture with three levels each. An unamended control was also included for each soil moisture level. The three soil moisture levels were as follows: dry soil with a gravimetric moisture content of 0.11 g g^{-1} soil; corresponding to the permanent wilting point (PWP) of a silt loam (Saxton & Rawls, 2006), equivalent to 24% water holding capacity (WHC); intermediate moisture content (0.17 g g^{-1} soil) which corresponds to 37% WHC, and moist soil at field capacity (0.23 g g^{-1} soil), corresponding to 50% WHC.

Prior to the incubation, each batch of soil was removed from the cold room and analyzed for moisture content as well as ammonium (NH_4^+) and NO_3^- (as described previously in Ch. 3: Main Study Materials and Methods). Soils were incubated in pre-labeled 16-ounce cups at 25 °C at the aforementioned soil moisture contents (24, 37, and 50% WHC). The samples for each replicate were prepared in separate batches.

For each sample, 300 g of oven-dry (OD) soil were weighed into a plastic bag and mixed thoroughly with the residue. The tomato residues were applied at an equivalent field application rate of 10 Mg ha^{-1}, which is the upper limit of vine biomass produced in trials at the sampling site. This resulted in application rates of 10.34 g of fresh residue, 4.36 g of partially dried, and 1.65 g of air-dried residues per 300 g of OD soil, which corresponded to an application rate of 92 mg residue N kg^{-1} OD soil applied. The same amount of N was added with the broccoli residues. This resulted in application rates of 6.49 g of fresh residue, 3.02 g partially dry residue, and 0.84 g air-dry residue per 300 g of OD soil.

After mixing the soil and residues, the samples were filled into the plastic cups and packed manually to a bulk density of approximately 1.3 g cm^{-3}. Using a side port needle, DI water was added evenly throughout the sample to reach the target moisture content of the

different treatments. The cups were covered with plastic wrap with air holes and placed into an incubator maintained at 25 °C. Moisture was monitored weekly by weighing the cups, and DI water was added with a pipette as needed to reach the target moisture content. The tomato residue incubation was carried out with 4 replicates per treatment, and the broccoli residue incubation with 3 replicates. After 1, 3, 6, and 12 weeks of incubation, cups were removed, sieved to 4 mm and analyzed for mineral N (NH_4^+-N and NO_3^--N).

N mineralization versus immobilization is defined as the soil mineral N content in the soil treatments when compared the control. An increase in N above control levels is considered mineralization, while that below is immobilization. Residue N mineralized was calculated by first subtracting the control mineral N concentration from the treatments', and the resulting N concentration was divided by the amount of residue N added to the soil.

Statistical analyses were performed as a two-way factorial with a completely randomized block design in R-Studio (v. 1.3.1093). Analysis of variance was performed to establish significant main effects and interaction effects, followed by post-hoc Tukey Tests to establish treatment effects. Differences were considered significant for $P < 0.05$. Residuals versus fitted and normal Q-Q plots served to determine if statistical assumptions were met. The datasets for the different dates and residues were analyzed separately. In the absence of a significant interaction between the two factors, the analysis focused on the main effects. With a significant interaction, the effects of a factor were analyzed at each level of the other factor.

5.3 Results

N Turnover from Tomato Residue Moisture and Soil Moisture at Three Levels

Initially, all the tomato residue treatments immobilized N compared to the unamended control as shown by lower mineral N content in the soil. Increasing residue moisture and soil moisture resulted in increased N immobilization (Figure 5.1). However, after the first week, the residue treatments began mineralizing N, and continued to mineralize N at each proceeding sampling date (Figure 5.1). Fresh residues initially immobilized significantly more N than the partially dry and air-dry treatments and mineralized less N until week six of the trial. After six weeks, the soil mineral N content in the 50% WHC soil moisture treatment had reached the level of the control. A significant interaction was detected between the residue moisture treatments and the soil moisture treatments (Figure 5.1, Table 5.2). The fresh residues mineralized significantly more N in the 50% WHC treatment when compared to the lower soil moisture treatments, while this increase was much less pronounced with the other two residue treatments (Figure 5.1). This interaction was no longer significant after twelve weeks. After twelve weeks of incubation, increasing soil moisture resulted in increased N_{min}, and residue moisture no longer had a significant effect (Figure 5.1, Table 5.2).

Averaged across all residue moisture treatments, the addition of tomato vine residues increased soil mineral N by 20 mg N kg^{-1} soil (41 kg N ha^{-1}), or approximately 21.6% of the applied residue N in the 50% WHC soil moisture treatment. The 50% WHC soil moisture treatment had the greatest amount of N_{min} of all the soil moisture treatments (Figure 5.1, Table 5.1). In soil held at the PWP, the soil mineral N levels of the amended treatments reached the level of the control by the end of the trial (Figure 5.1).

Table 5.2: ANOVA and pairwise comparison results for tomato residue incubation. The top three rows (white) feature ANOVA P-value results. The bottom six rows (grey) show percent of residue N mineralized, averaged across treatments. Negative values indicate net N immobilization compared to the control. Letter superscripts indicate significant differences in the main effect. The 24% WHC soil moisture treatment is equivalent to permanent wilting point (PWP) as referred in the text. * indicates treatments involved in significant interactions.

Treatment	Week 1	Week 3	Week 6	Week 12
Soil Moisture (S)	<0.001	0.1952	<0.001	<0.001
Residue Moisture (R)	<0.001	<0.001	<0.01	0.167
S*R Interaction	0.553	0.912	<0.01	0.448
50% Soil Moisture	-16.1 [a]	-9.4 [a]	7.2 [b*]	21.6 [b]
37% Soil Moisture	-11.3 [b]	-5.7 [a]	-1.2 [a]	3.5 [a]
24% Soil Moisture	-7.4 [c]	-6.0 [a]	-4.3 [a]	-0.1 [a]
Fresh Residue	-16.4 [a]	-14.5 [a]	-2.4 [a*]	6.7 [a]
Partially Dry Residue	-10.5 [b]	-4.7 [b]	2.9 [b]	7.4 [a]
Air-Dry Residue	-7.9 [b]	-1.9 [b]	1.3 [b]	10.9 [a]

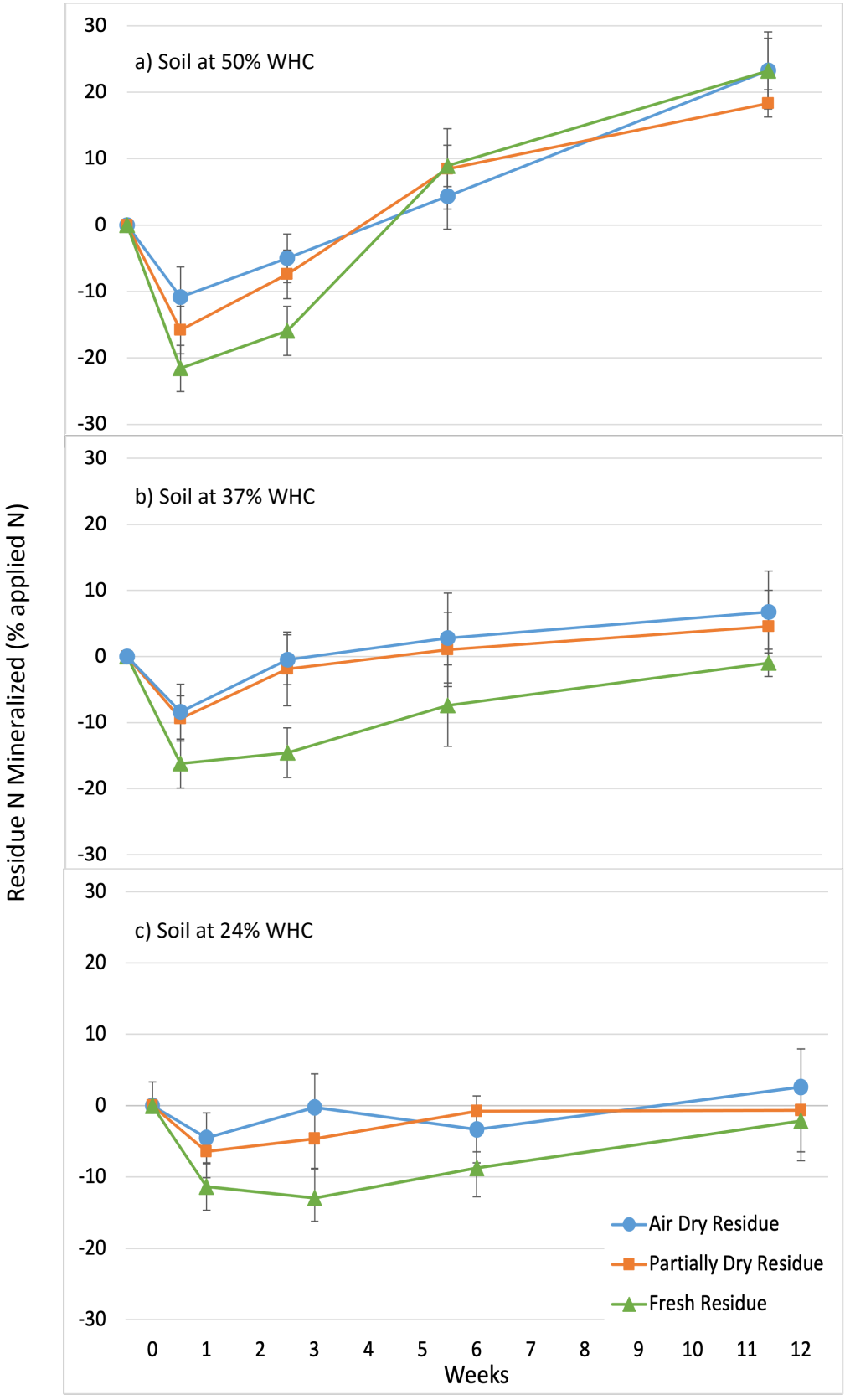

a) Soil at 50% WHC
b) Soil at 37% WHC
c) Soil at 24% WHC
Residue N Mineralized (% applied N)
30
20
10
0
-10
-20
-30
0 1 2 3 4 5 6 7 8 9 10 11 12
Weeks
Air Dry Residue
Partially Dry Residue
Fresh Residue

Figure 5.1. Net mineralization of nitrogen (N) from tomato residue incubated at 25 ºC for twelve weeks. Features soil moisture contents at a) 50% water holding capacity (WHC), b) 37% WHC, c) 24% WHC (corresponding to permanent wilting point (PWP)). The three residue moisture contents were air dry (7% moisture content), partially dry (65% moisture content), and fresh (85% moisture content). Error bars indicate standard error. Units are in percent of applied residue N mineralized.

N Turnover from Broccoli Residue Moisture and Soil Moisture at Three Levels

All of the broccoli residue treatments began mineralizing N immediately as shown by the increase in soil mineral N in all residue treatments when compared to the unamended control and continued to do so for the duration of the trial (Figure 5.2). Initially, only residue moisture had a significant effect on N_{min}. Within the residue moisture treatments, the fresh residues mineralized significantly less residue N than the partially dry and air-dry residues, while the partially dry residue treatment mineralized the most residue N (Table 5.3, Figure 5.2). After the first week, residue moisture was no longer significant for the remainder of the trial. At week twelve, the 50% soil moisture treatment had significantly increased soil mineral N content (Table 5.3, Figure 5.2). No interaction between residue moisture and soil moisture was found.

Averaged across all residue moisture treatments, the addition of broccoli residues increased soil mineral N by 44 mg N kg^{-1} soil (90 kg N ha^{-1}) in the 50% WHC soil moisture treatment, corresponding to approximately 50% of the applied residue N being mineralized. The fresh residue moisture treatment resulted in the greatest soil mineral N content of the three residue moisture treatments by the end of the trial, with decreasing residue moisture resulting in decreased soil mineral N content, though the difference was not statistically significant (Table

5.3). The 50% WHC soil moisture treatment had the greatest amount of N_{min} of all the soil moisture treatments by the end of the trial (Figure 5.2, Table 5.3). The soil at the PWP mineralized the least residue N, resulting in a decrease of residue N mineralized by 12 percentage points when compared to the 50% WHC treatment, equating to a difference of approximately 31 mg N kg^{-1} soil (64 kg N ha^{-1}). There were no significant differences in mineral N content between the 37% and PWP soil moisture treatments by the end of the trial (Figure 5.2, Table 5.3).

Table 5.3: **ANOVA and pairwise comparison results for the broccoli residue incubation.** The top three rows (white) feature ANOVA P-value results. The bottom six rows (grey) show percent of residue N mineralized, averaged across treatments. Letter superscripts indicate significant differences in the main effect. The 24% soil moisture treatment corresponds to the permanent wilting point (PWP) referred to in the text.

Treatment	Week 1	Week 3	Week 6	Week 12
Soil Moisture (S)	0.679	0.059	0.237	< 0.01
Residue Moisture (R)	< 0.001	0.943	0.650	0.860
S*R Interaction	0.752	0.911	0.665	0.726
50% Soil Moisture	22.8 [a]	39.5 [a]	44.4 [a]	50.2 [b]
37% Soil Moisture	27.5 [a]	30.4 [a]	33.1 [a]	30.8 [a]
24% Soil Moisture	22.1 [a]	27.0 [a]	36.9 [a]	38.1 [ab]
Fresh Residue	16.4 [a]	32.6 [a]	36.7 [a]	41.3 [a]
Partially Dry Residue	31.4 [b]	31.3 [a]	41.6 [a]	39.2 [a]
Air Dry Residue	24.6 [b]	32.9 [a]	36.1 [a]	38.7 [a]

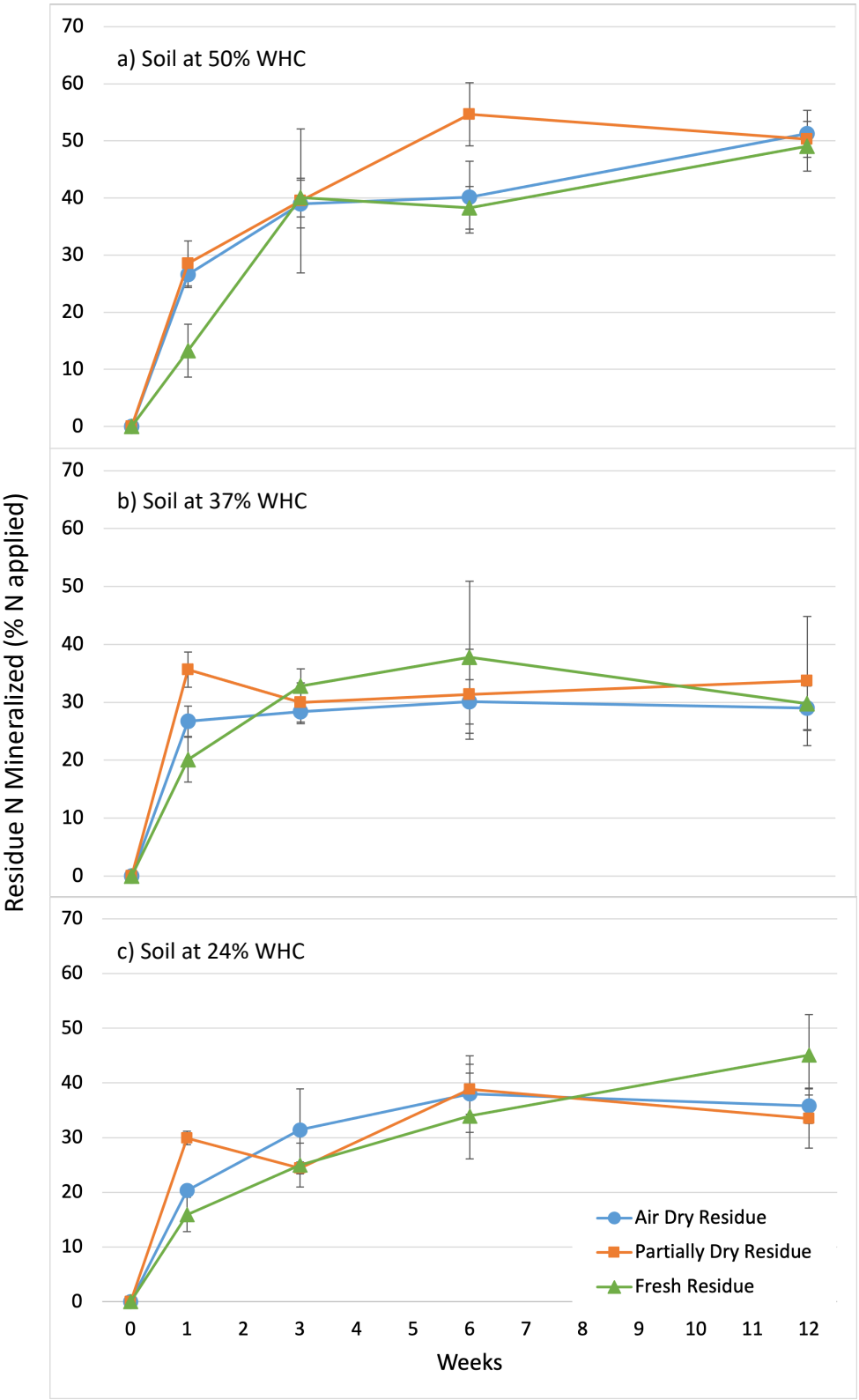

a) Soil at 50% WHC
b) Soil at 37% WHC
c) Soil at 24% WHC
Residue N Mineralized (% N applied)
Weeks
Air Dry Residue
Partially Dry Residue
Fresh Residue
0
10
20
30
40
50
60
70
0
1
2
3
4
5
6
7
8
9
10
11
12

Figure 5.2. Net mineralization of nitrogen (N) from broccoli residue incubated at 25 ºC for twelve weeks. Features soil moisture contents of **a)** 50% water holding capacity (WHC), **b)** 37% WHC, **c)** 24% WHC (corresponding to permanent wilting point (PWP)). Three residue moisture contents featured: air dry (7% moisture), partially dry (74% moisture), and fresh (88% moisture). Error bars indicate standard error. Units are in percent of applied residue N mineralized.

By the end of the incubations, approximately 22% and 50% of the tomato and broccoli residue N was mineralized, respectively, in the soil with the highest moisture content. This is equivalent to 41, and 90 kg residue N ha^{-1}, respectively. This is a considerable amount of N, which accumulated predominantly as nitrate-N. Though, while the incubations studies were performed under varying moisture contents, they were held at a constant temperature and thus may not represent N turnover under field conditions.

5.4 Discussion

We hypothesized that (1) soil moisture will have a stronger effect on net N_{min} than residue moisture and that (2) the effects would be more pronounced with broccoli residues, as they have a narrower C:N ratio and faster N_{min} rate as stated by De Neve & Hofman (1996).

The results presented above partially support these hypotheses. When observing the short-term effects of soil moisture, we partially reject the first hypothesis for both the tomato and broccoli residue treatments. For the broccoli residue trial, soil moisture didn't have a significant effect on residue N_{min} until week twelve. For the tomato residue trial, residue moisture and soil moisture significantly affected N_{min} until week six. Because residue moisture significantly affected N_{min} until week six in the tomato incubation, the effect of residue moisture was more

pronounced than in the broccoli incubation where residue moisture was no longer significant after week one. Allowing us to also reject the second hypothesis in regard to short-term effects of tomato versus broccoli residue moisture on N_{min}.

However, in the long-term, we accept the first hypothesis for both residue treatments where only soil moisture was found to be significant by week twelve. By the final week of the incubation, there was a significant and measurable difference in the levels of N_{min} between soil moisture treatments, but residue moisture was no longer significant. The long-term effect of soil moisture on N_{min} was expected and is supported by previous research on the effect of soil moisture on N_{min} (Cassman & Munns, 1980; Klemedtsson, Svensson, & Rosswall, 1988; Myers, Weier, & Campbell, 1982; Quemada & Cabrera, 1997). A linear relationship between mineralized N and soil water content was established by Stanford and Epstein (1974).

For the long-term data, the second hypothesis that the N_{min} effects with increasing with increasing soil moisture would be more pronounced with broccoli residues was also accepted. This is due to the addition of broccoli residues resulting in in much greater amounts of mineral N in the 50% WHC soil moisture treatment by the end of the incubation than the tomato residue treatments. The fact that residue moisture resulted in significant differences in N turnover trends initially indicates that residue moisture only plays a role in short-term N turnover, but that soil moisture ultimately determines long-term N availability.

A potential explanation for the diminishing effect of residue moisture on N_{min} over time could be that the air-dry and partially dry residue treatments were absorbing moisture from the surrounding soil and eventually reached similar moisture contents as the fresh residues. This is due to what Kutlu et al. (2018) refers to as the "sponge effect" wherein the strong capillary forces within the residue absorb moisture from the surrounding soil. In their study, air-dried

residues absorbed enough moisture from the surrounding soil (which was at 30% water-filled-pore-space, equivalent to a gravimetric water content of 0.15 g H_2O g^{-1} OD soil) until they reached full saturation. Water absorption characteristics and thresholds varied between corn (*Zea mays*) and soybean (*Glycine max*) residues. A similar trend was observed in a study by Quemada and Cabrera (2002) where oat straw (*Avena sativa*) exhibited higher water retention characteristics than wheat straw (*Triticum aestivum L.*). The authors of both studies hypothesized that this is due to residue quality differences such as lignin and carbohydrate content, which play a crucial role in residue water absorption capacity by influencing the matric potential of the residues. This conclusion was supported by Dirks et al. (2010) who also found that higher lignin:N ratios reduced a residue's ability to absorb water vapor. In our study, the tomato residues had a lignin:N ratio of 2.4, which was higher than the lignin:N ratio of 0.8 in the broccoli residues. This may have affected the residues' ability to absorb water from the surrounding soil. This difference in water absorption capacity could explain why the tomato residue moisture had a prolonged significant effect on N_{min}. In contrast, residue moisture was only significant in the broccoli residue moisture treatments for the first week, as those residues potentially absorbed moisture more quickly from the surrounding soil, leading to rapid decomposition.

The incorporation of tomato residues into soil at high soil and residue moisture content resulted in increased net N immobilization (observed during weeks one through three). The initial N immobilization when compared to the control and initial N content was not expected, as the tomato residues had a C:N ratio of 19:1. Generally, the defining cutoff lies at a C:N ratio of approximately 20:1 (Frankenberger & Abdelmagid, 1985). A C:N ratio below 20:1 is expected to mineralize N immediately (Frankenberger & Abdelmagid, 1985). Our data suggests that this

threshold may be too high. Initial N immobilization with incorporated tomato residue has also been observed in the field (Chapter 4 of this thesis).

The increased N immobilization early on with increasing residue moisture and soil moisture has also been found in other studies. Thapa et al. (2021) found that at the highest water potential treatment (-0.03 MPa, equivalent to 0.221 g H_2O g^{-1} OD soil), early N immobilization was greatest compared to all other water potential treatments (ranging from -10.0 to -0.03 MPa) for rye residues (*Secale cereale* L), which had a C:N ratio of 87.7. They hypothesized that this was because the rye had a high fiber content and C:N ratio and that microbial decomposition was greatest under those conditions. The N immobilized from the rye was later released and by the end of their trial after 168 days, 11% of rye residue N had been mineralized. We observed the same trend in our study with tomato residues.

In the broccoli trial, the lower N_{min} in the fresh residue moisture treatment compared to the lower residue moisture treatments during the first week was surprising (Figure 5.2, Table 5.3). It was expected that increased residue moisture would result in increased microbial activity and a corresponding high N_{min} with fresh residues, much like the fresh tomato residues showing increased N immobilization. One potential explanation for this could be that high microbial activity depleted oxygen in microsites, resulting in anaerobic conditions, which in turn led to denitrification losses. This effect was likely temporary as it was no longer observed after the first week. Quemada and Cabrera (1997) observed a decrease in N_{min} when their clover residue (C:N of 28.7) treatment approached a soil moisture content of -0.03 MPa at the highest temperature treatment of 35 ºC (equivalent to 0.116 g H_2O g^{-1} OD soil, or 55% water-filled-pore-space (WFPS)) in a sandy-loam, and hypothesized that the effect was due to enhanced anaerobic microsites or denitrification from increased temperature.

In both the tomato and broccoli residue incubations, N_{min} was significantly reduced but did not stop in the soil maintained at PWP. These results imply that even at very low moisture contents, soil microorganisms continue to mineralize N, though slower than at higher soil moisture contents. This is supported by a study by Dirks et al. (2010) who found that decomposer microorganisms remained active even at extremely low relative humidity contents (below 60% and approaching 0% relative humidity). In their study, water vapor in the form of fluctuating atmospheric relative humidity was the only source of moisture for their litterbag decomposition study in a Mediterranean shrubland. They observed that during the dry season, local litter lost between 4-18% of its mass over a rainless four-month period. While they attributed water vapor, solar radiation, and litter quality as the main causes in the degree of decomposition observed, they found that 95% of the variation was explained by water-vapor absorption from the litter. Kutlu et al. (2018) also stated that in dry soil, residues that have absorbed moisture from the surrounding soil serve as microsites for decomposition and nutrient cycling, which was likely the case in our study as well. Furthermore, Thapa et al. (2021) found that even as water potential fell below -10.0 MPa (equivalent to 0.033 g H_2O g^{-1} OD soil), microbial decomposition continued to occur.

For growers and producers moving towards more water-efficient methods of irrigation, particularly drip irrigation, these results show that while N_{min} is greatest at field capacity, the driest parts of the soil are continuing to mineralize and supply plant-available N. Residue moisture did not continue to significantly affect N_{min}, this implies that regardless of residue moisture levels upon incorporation, there is no increased risk of nitrate leaching. However, there is potential for nitrate leaching depending on the crop type incorporated.

5.5 Conclusion

Over the twelve weeks of the incubations, the incorporation of tomato and broccoli residues resulted in net N_{min} when compared with the unamended control. Nitrogen mineralization increased as soil moisture content increased and approached field capacity. However, even at the lowest soil moisture content, which corresponded to the PWP, N_{min} took place, though slower than at higher soil moisture contents. This implies that even in dry soils, soil microorganisms are still active. In contrast, the moisture content of the residues only had a short-term effect. These results indicate that residue moisture at the time of incorporation will not impact N_{min} in the long term. Therefore, letting residues dry on the soil surface before incorporation does not seem to be an effective practice to reduce the amount of residual soil nitrate present during the winter months. For broccoli residues in particular, there is an increased risk of nitrate leaching during the winter months due to rapid decomposition and N_{min}.

6. Conclusion and Closing Remarks

Our main study explored regional N_{min} variability and established particulate organic N and silt content as important soil properties influencing N_{min} in the northern California Central Valley. It also confirmed that soil moisture drives N cycling, even at very low moisture content. The field trial and incubation of different residues allowed us to compare N turnover across seven different residues, which resulted in cotton residues mineralizing the most N, and sunflower residues immobilizing the most N when compared to the control. The residue and soil moisture incubation studies provided results to improve our understanding of the influence of residue quality and soil moisture on N release and turnover for tomato and broccoli residues. In the short term, residue moisture significantly affected N mineralization, but by the end of the

trial was no longer having an effect. In the long term, increasing soil moisture resulted in greater N mineralization. However, even the lowest soil moisture treatment continued to mineralize N.

This research overall has helped us, and our local farm advisors and farmers, develop a more complete understanding of N_{min} dynamics in the studied regions. Moving forward with this knowledge we are now better prepared for the next steps in our research. These include improving upon and validating the models developed for these regions with field trials and developing N uptake curves for common crops, as well as further investigation into the composition of residual SOM using Fourier transform infrared spectroscopy and its role in N availability.

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