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Regional considerations for phosphorus and carbon management

By

NADIA MOUKANNI
DISSERTATION

Submitted in partial satisfaction of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

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OFFICE OF GRADUATE STUDIES

of the

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DAVIS

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Abstract

Considerable uncertainty exists on the topic of soil organic carbon (SOC) sequestration in agroecosystems with Mediterranean climate due to the wide range in practices, crops, and soils . These vulnerable yet productive agroecosystems are characterized by low soil organic carbon content. Thus, these soils are considered potential sinks to sequester SOC. To efficiently stabilize SOC, it is well established that the main mechanisms of SOC stabilization and destabilization across soil depths are edaphic factors that affect soil management practices. The first chapter of this dissertation focused on reviewing the main mechanisms of soil organic carbon stabilization within different fractions of soil organic matter, particularly, particulate organic matter (POM) and mineral associated organic matter (MAOM) with the aim of optimizing C sequestration through soil management practices, such as cover cropping. The impact of different cover crop management practices such as species selection, termination time and termination method on long term SOC stabilization are discussed. This chapter sheds light on future research avenues to provide more informed decisions on cover crop management practices that target SOC sequestration in croplands with Mediterranean climate.

Given the complexity of soil biogeochemical functions and the escalating need to manage soils for multiple outcomes, we focused on another key nutrient required by plants, which is Phosphorus (P). P has multiple benefits spanning from the metabolic scale, where P plays a crucial role as an energy carrying molecule to its largest role increasing plant yield and root proliferation. Hence, the second chapter focuses on investigating the possibility to use readily available and easy-to-measure soil data such as soil color, clay, and SOC to estimate P sorption index (PSI), which is considered as an important parameter to rationalize P amendments and avoid the environmental risks related of surface water eutrophication, which is primarily due to P overfertilization. Our results showed that there is a great potential to use readily available soil

data to predict P sorption capacity. Soil color parameters, soil redness (*a*) and soil yellowness (*b*) were found to be closely related to PSI as well as clay content and SOC content. Regression models built using the aforementioned set of predictors performed reasonably well when considering all soil types including Entisols, Mollisols, Vertisols, Alfisols and Ultisols (R^2=0.62). The model fit increased (R^2= 0.72) when highly developed soils with very high PSI were removed. Results suggest there is great potential to capitalize on the use of standard measurements from characterization by laboratories and observations from the field or soil survey to guide regional patterns in P sorption and availability.

Lastly, the third chapter of this dissertation highlights the regional variability of soils' capacity to stabilize SOC within the fine fraction. In this chapter, we explored variability in soil C saturation deficit, defined as the difference between the theoretical maximum C and current C stored within MAOM along a chronosequence of soils having variable degree of soil development (weakly developed soils of the alluvial fan, moderately developed soils in low terraces, and highly developed soils in high terraces). Results showed a remarkable difference in soil C saturation deficit between the three soil regions, the key difference being mass proportion of fine fraction (clay and silt), and the dominant clay mineralogy. Soils having significantly higher clay and silt with predominantly 2:1 clays had significantly higher soil C saturation deficit. Furthermore, our results showed that for soils far from the saturation limit, increases in soil C inputs didn't significantly alter soil C saturation deficit. However, for soils saturated or nearly saturated with C, the addition of carbon significantly reduced soil C saturation deficit. Important variation in the most reactive SOC fractions (coarse POM_c, fine POM_c, and $MAOM_c$) were observed along the soils of the chronosequence having variable degree of soil C saturation

deficit. These results emphasize the importance of place-based soil management practices depending on the unique soils’ inherent properties in order optimize soil C sequestration.

Chapter 1 Optimizing carbon sequestration through cover cropping in Mediterranean agroecosystems: synthesis of mechanisms and implications for management (Moukanni et al., 2022).

1.1 Abstract

Semiarid Mediterranean ecoregions are characterized by low soil organic carbon content and large potential to become a carbon sink when appropriately managed. Soil carbon sequestration may also play an important role in improving the resilience of these vulnerable agroecosystems to increasingly drastic impacts of global climate change. One agricultural practice that aims to increase soil organic carbon stocks, among other beneficial outcomes, is the use of cover crops. Although cover crops can increase soil organic carbon content, recent studies have observed that cover crops may lead to lower soil carbon stocks when considering co-management strategies, especially at greater soil depths. In this review, we outline the current paradigm of soil organic carbon dynamics and aim to apply our current understanding of soil carbon sequestration processes to cover crop management. We review how cover crop practices such as species selection, growth duration, and termination methodologies may impact soil organic C sequestration and stabilization processes and provide insights to direct future research and inform cover crop management for C sequestration in Mediterranean agroecosystems.

1.2 Introduction

The world's attention is gaining focus on possible ways for agriculture to offset the impacts of global climate change (Lal, 2016). Soils have the unique potential to sequester large amounts of carbon (C). Soils contain approximately 75% of the terrestrial carbon pool, which corresponds to two to three times the amount of C in both the atmosphere and vegetation (Fontaine et al., 2007; Schmidt et al., 2011; Scharlemann et al., 2014). Thus, with about half of habitable land-use being allocated to agriculture (Ellis et al., 2010), agricultural soils play a key role in maintaining a balanced global carbon cycle and provide mitigation and adaptation strategies to address global climate change (Gross and Harrison, 2019; Tautges et al., 2019; Lavallee et al., 2020;).

Occupying nearly 15% of the global land area, soils in Mediterranean climates have the potential to be significant carbon sinks (Safriel et al., 2005). Having cool moist winters and warm dry growing seasons (Aguilera et al., 2013), these soils are typically low in soil organic carbon (SOC) due to limited primary productivity and conditions that favor rapid microbial decomposition of plant residue (Van-Camp et al., 2004; Chiti et al., 2012; Wiesmeier et al., 2013). However, agricultural practices remove some of these limitations by increasing biomass inputs and therefore C storage potential if managed adequately.

Soils of Mediterranean environments are also highly biodiverse (Underwood et al., 2009) and provide natural resources to support some of the most productive agroecosystems in the world (Guan et al., 2009) in regions of California, central Chile, southwest Australia, southwest South Africa, and land around the Mediterranean Sea (Aschmann, 1984; Aguilera et al., 2013). In fact, the state of California supports the production of more than half of the US fruits, nuts, and vegetables (Johnston and Carter, 2000). Adoption of irrigated agriculture in these designed landscapes impact many of the processes regulating carbon deposition and cycling, such as enhancing biomass inputs to soil. However, intensification, simplified rotations, and soil disturbances have hampered this potential despite the recognized benefits of conservation practices for SOC accumulation (Lal, 2020). Given the C sequestration potential of Mediterranean soils and the potential for widespread soil degradation in these agroecosystems, there is an urgent need to identify effective management approaches that optimize soil organic carbon sequestration and stabilization in these unique agroecosystems.

Cover cropping has been recognized as an effective practice to promote soil conservation with co-benefits for sustainability and resilience of agriculture (Duval et al., 2016; Novara et al., 2021) through erosion control, and nutrient and water conservation (Shroder, 2020). Cover crops can be grown as grazed or exported forage, nutrient catch crops, ground cover to reduce losses, and green manure when used as a source of nutrients (Shackelford et al., 2019). As such, cover crops are widely promoted through EU Common Agricultural Policy (Shackelford et al., 2019) and federal and state incentive programs in the US. Cover cropping is also increasingly recognized as a practice that increases SOC (Gristina et al., 2020). However, uncertainties and high variability in the impacts of cover crops on SOC stocks remain. While various meta-analyses have indicated that cover crops can increase SOC content (Aguilera et al., 2013; Poeplau and Don, 2015), other studies show no effects (Kaspar et al., 2006; Celette et al., 2009; Steele et al., 2012; Oliveira et al., 2016) and even loss of SOC in the deep soil horizons of some agroecosystems (Tautges et al., 2019; Camarotto et al., 2020). The effectiveness of cover cropping is therefore site-specific and varies with soil properties, climate, and management practices (García-Orenes et al., 2010; Peregrina et al., 2010; Ramos et al., 2010; Gómez, 2017). Recent understanding of carbon and nutrient flows in soil ecosystems also point to the importance of cycling through microbial communities for long term carbon sequestration (Lehmann and Kleber, 2015; Kallenbach et al., 2016). Thus, the emerging complexities of SOC cycling, and stabilization and destabilization mechanism must inform cover crop management to maximize C sequestration (Harden et al., 2018) and more accurately predict cover crop management outcome (Dijkstra et al., 2021).

The goal of this review is to apply our current understanding of SOC pools and fluxes to guide cover crop management strategies that prioritize SOC sequestration. To contextualize this discussion, we constrained this review to studies of cover cropping in systems with Mediterranean-type climates. These agroecosystems are complex and include a wide range of commodities (perennial and annual crops) and large variability in agricultural practices that affect cover crop management and SOC dynamics. Cover crop management goals are also diverse in these settings – including a source of crop nutrients, to control erosion, improve soil health, promote biodiversity, and offset greenhouse gas emissions – with each objective influencing how cover crops are selected and managed. We first review a set of grounding principles to appraise SOC stabilization and destabilization mechanisms in these systems based on three influencing factors: (1) SOC cycling; and influence of (2) soil depth; and, (3) plant residue quality. We then discuss how considering SOC pools and storage mechanisms across depths and for various biomass inputs can provide insight into cover crop management (i.e., species selection, growth duration, and termination methodology) for increased SOC sequestration.

1.3 Considering SOC as complex pools and dynamic fluxes of carbon

Understanding SOC dynamics in response to land-use changes, soil management practices, and global climate change will help identify opportunities to optimize SOC sequestration and ensure its long-term persistence. Scientific research has well established the drawbacks associated with considering soil organic matter (SOM) as a single uniform entity (Parton et al., 1988; Jenkinson et al., 1990; Trumbore, 2009). More recent conceptual frameworks have developed upon our understanding of SOM dynamics, specifically the physicochemical complexity of SOC and its continuum as pools (storage) and fluxes (inflow and outflow rate) components across a spectrum of decomposition stages, each with contrasting properties (Six et al., 2002; Cotrufo et al., 2013; Lehmann and Kleber, 2015; Basile-Doelsch et al., 2020; Lavallee et al., 2020; Zhu et al., 2020). Nevertheless, our understanding of the specific determinants underlying the long-term persistence of SOC are currently under contention. Recent conceptual frameworks are broadly moving away from models based on chemical recalcitrance mechanisms, such as humic substances with degradative resistance, toward models based on chemical stabilization and physical protection mechanisms of SOM via mineral sorption and aggregate occlusion (Figure 1.1) (Six et al., 2002; Lehmann and Kleber, 2015; Basile-Doelsch et al., 2020; Witzgall et al., 2021). Ultimately, the most significant challenge remains in categorizing and measuring this dynamic SOC continuum; especially when considering that the formation of stable and long-term sequestered SOC requires continual flux and turnover (Six et al., 2002; Janzen, 2006; Kallenbach et al., 2016; Dynarski et al., 2020).

Recently developed SOC cycling theories propose that, upon deposition into the soil, plant and animal-derived organic material of diverse sizes, quality, and molecular complexity are continuously processed by the soil decomposer community, through fragmentation and depolymerization, eventually resulting in the lower molecular-weight and labile substrates that are utilized during microbial assimilation (Cotrufo et al., 2013; Lehmann and Kleber, 2015; Liang et al., 2017; Basile-Doelsch et al., 2020).

Compared to larger organic fragments, these simple and labile biopolymers and monomers have both a higher oxidation state and increased solubility in water, thus increasing their transport and reactivity within the soil solution. In turn, this dissolved organic matter (DOM) is generally more spatially accessible (Erktan et al., 2020) with a higher capacity for assimilation into microbial biomass due to its smaller size and lower molecular weight (Weiss et al., 1991; Kallenbach et al., 2015). Simultaneously, the solubility and heightened oxidation state of these labile carbon substrates are thought to facilitate more sorption interactions with mineral surfaces, increasing their protection and persistence through stabilization within the soil matrix and/or incorporation within aggregates (Cotrufo et al., 2013; Robertson et al., 2019). While this microbial metabolic processing of substrates results in some loss of SOC through respiration, it also facilitates the flux of C through the soil via production of microbially-derived substrates and turnover of microbial necromass -- a concept known as the microbial carbon pump (MCP) (Liang et al., 2017; Liang, 2020; Zhu et al., 2020). Thus, under this concept, C inputs have several possible pathways: (1) continual flux through the MCP; (2) escape from the MCP through microbial respiration; or (3) escape from the MCP via physicochemical protection of microbial necromass within the soil matrix and/or occlusion within aggregates.

Importantly, organic substrates exist along a thermodynamic gradient whereby the transformation of large molecular weight, recalcitrant, and energy-rich compounds into smaller molecular weight, labile, and energy-poor compounds release energy and reduce the activation energy required to depolymerize subsequent stages (Malik et al., 2016). This has functional relevance since the enzymatic investment requirements of the soil microbial community to process soluble, labile substrates is much less than for processing recalcitrant, high-energy compounds such as cellulose and lignin. As such, alterations in the quality of C inputs into soil may cause shifts in the microbial community’s energy investment strategies (Schimel et al., 2007; Kallenbach et al., 2015; Kravchenko et al., 2019; Malik et al., 2020), as well as their Carbon Use Efficiency (CUE) and thus the fate of C inputs (Manzoni et al., 2012; Cotrufo et al., 2013; Kirkby et al., 2013; Kallenbach et al., 2015). Extracellular enzyme production and increased metabolic costs associated with breakdown of complex biopolymers have been shown to reduce CUE when compared to labile DOM compounds, which may be assimilated into microbial biomass with minimal depolymerization (Lekkerkerk et al., 1990; Malik et al., 2016). The higher nitrogen (N) content of the DOM pool may also facilitate more efficient utilization, requiring less microbial investment in nutrient acquisition (Berg and Meentemeyer, 2002; Hessen et al., 2004; Liang et al., 2007; Liang et al., 2019). As such, it has been hypothesized that labile C substrates are the dominant source of microbial products, while also having a more direct and efficient pathway toward mineral stabilization (Cotrufo et al., 2013; Kallenbach et al., 2015). In general, cover cropping is understood to increase the proportion of labile carbon inputs into soil (Duval et al., 2016; White et al., 2020). However, less attention has been paid to the specific ways by which cover crop management strategies may increase the relative proportion of plant photosynthates allocated toward labile dissolved carbon inputs, such as through enhanced rhizodeposition, and how this may therefore result in improved SOC accumulation.

With respect to the monitoring of SOC persistence, a framework, proposed in Lavallee et al. (2020), suggests a simple and ecologically relevant method for measuring SOC storage that separates SOM into two physically defined pool fractions, particulate organic matter (POM) and mineral-associated organic matter (MAOM). There is potential for cover crop selection and management to influence the size of these fractions. Also called the light fraction, POM is formed during litter decomposition through fragmentation and depolymerization. It contains lightweight fragments of plant and fungal material, composed predominantly of complex structural compounds such as celluloses, lignin, and chitin, that are relatively undecomposed and generally low in nutrient content (Six et al., 2001; Kögel-Knabner et al., 2008; Sanderman et al., 2014; Cotrufo et al., 2015). POM exists within a spectrum of size and density categories and may either be physically accessible for decomposition (free) or protected from degradation through occlusion within aggregates (Jastrow and Miller, 1996; Lavallee et al., 2020). Significant research has concluded that POM is essential in the genesis of large microaggregates and macroaggregates, as a nucleus for the assemblage of smaller microaggregates together (Cambardella and Elliott, 1993; Jastrow and Miller, 1996; Angers et al., 1997; Six et al., 2000; Bongiovanni and Lobartini, 2006; Jastrow et al., 2007; Witzgall et al., 2021). As such, the role of POM in the formation of soil structure and SOC physical occlusion is significant. The physical transport pathways of POM are notably more limited than that of DOM substrates, and so its incorporation within the soil profile occurs more slowly in lieu of cultivation and bioturbation (Rabbi et al., 2014; Cotrufo et al., 2015).

On the other hand, MAOM contains low molecular weight compounds derived mainly from microbial decomposition (Kögel-Knabner et al., 2008; Cotrufo et al., 2013; Sanderman et al., 2014; Castellano et al., 2015; Kleber et al., 2015). The extent of MAOM accumulation in soils is dependent on the balance between production of microbial biomass and decomposition to necromass (Six et al., 2006). This balance is influenced by the microbial CUE , which is defined as the proportion of organic C allocated toward the accumulation of biomass (anabolism) relative to the organic C allocated toward respiration (catabolism) (Spohn et al., 2016). Thus, higher CUE leads to higher microbial biomass, and therefore, higher SOC cycling and storage from necromass, while lower CUE leads to more carbon respiration and gas losses (Manzoni et al.,2012).

The microbial biomass (necromass) produced is then stabilized into the MAOM pool mainly through physicochemical interactions with soil minerals (Figure 1.1) (Six et al., 2002; von Lützow et al., 2007; Cotrufo et al., 2013; Kallenbach et al., 2016). Hence, the capacity of a soil to store SOC as MAOM is conditioned by the inherent soil physicochemical characteristics, such as the relative ratio of clay and silt content, clay mineralogy (i.e., 1:1 or 2:1 phyllosilicates), pH, short-range ordered minerals, and the presence of crystalline and poorly crystalline Fe/Al oxides that combine to determine mineral surface area and sorption and desorption dynamics (Six et al., 2002; Jastrow et al., 2007; Bailey et al., 2019). Thus, soils have different SOC mineral saturation potentials, defined as the theoretical maximum of SOC storage within the MAOM under optimum conditions (i.e. soil moisture, temperature, continuous carbon inputs, and soil mineralogy) (Castellano et al., 2015).

This differing SOC saturation potential was highlighted in a recent comparative study that aimed to quantify the potential of SOC sequestration of a wide range of soil functional groups in the World Reference Base (i.e., calcaric, calcic, fluvic, and vertic) as a result of cover cropping. All the soils studied exhibited different C sequestration potential, where soils with fluvic diagnostic materials (marine and lacustrine parent materials) showed the highest SOC storage potential (34.4 t/ha) at 0-30 cm soil depth (Gristina et al., 2020). The concept of saturation limit predominately concerns the MAOM pool, with some studies indicating no saturation limitations for POM (Six et al., 2002; Stewart et al., 2009; Lajtha et al., 2014). Given that at least half of the total SOC in arable land consists of the MAOM pool (Kirchmann et al., 2004; Miltner et al., 2012; Plaza et al., 2013; Wiesmeier et al., 2013), it may be most impactful to target soil C increases within the MAOM. However, several studies suggest that once the MAOM fraction is saturated, the SOC accrual increase in the POM fraction becomes larger (Six et al., 2002; Castellano et al., 2015; Cotrufo et al., 2019).

Most notably, POM and MAOM have highly variable mean residence times. While the POM fraction generally resides from years to decades, MAOM has longer residence time potentials of decades to centuries (Kögel-Knabner et al., 2008; Kleber et al., 2015). Though distinct in their chemical composition (Cotrufo et al., 2015), the residence times of POM and MAOM are thought to be related more to their physical protection mechanisms in soil, and thus, when physically protected through macroaggregate occlusion, POM may persist on timescales of decades to centuries (von Lützow et al., 2007). However, macroaggregates are less persistent than smaller microaggregates and are thought of as highly susceptible to breakdown upon soil disturbance. Given the context of our need to monitor SOC sequestration and the challenge of identifying meaningful and accurate indicators of SOC change over time, POM (both free and occluded) and MAOM are understood to be distinct and relevant measurements for evaluating the responses of SOC to contrasting agricultural management practices. They are also relevant in considering physical stabilization mechanisms, with approachable measurability and broad applications for landscape modeling of cover crops and SOC sequestration rates across semi-arid regions (Cambardella and Elliott, 1993; Collins et al., 1999; Duval et al., 2013; Rocci et al., 2021).

With further relevance to semi-arid cropland, having regionalized knowledge of SOC sequestration potentials (saturation deficit) for each pedoclimatic condition would help effectively assess the capacity of soils to store more C and inform cover crop management for C sequestration (Castellano et al., 2015; Cotrufo et al., 2019; Gristina et al., 2020; Devine et al., 2021). In fact, soils can be saturated even when SOC is low, due to limitations of SOC stabilization imposed by management and climate (Stewart et al., 2007). As a result, an increase in C inputs would not necessarily increase the total and/or physico-chemically stabilized SOC stocks (Castellano et al., 2015). In fact, some soils can exhibit a negative balance of SOC due to the occurrence of some destabilization mechanisms such as desorption of the previously adsorbed SOC (Figure 1.1) (Schmidt et al., 2011). Once SOC is detached from soil minerals, it becomes more available for decomposition, mineralization, microbial assimilation and eventually release to the atmosphere as CO2 (Figure 1.1) (Novara et al., 2016).

1.4 Considering SOC stabilization and destabilization mechanisms in deeper horizons.

Recent studies have demonstrated that low concentrations of organic C in deep soil layers equate to large SOC stocks when integrated across the entire soil profile (Richter and Markewitz, 1995; Rumpel and Kögel-Knabner, 2011; Harper and Tibbett, 2013; Moreland et al., 2021), with more than half of the total SOC stored in deep soil layers beyond the top 20 cm (Jobbágy and Jackson, 2000; Harrison et al., 2011; Schmidt et al., 2011). The SOC storage dynamics in deep soil layers are regulated by the lack of consistent fresh C inputs, and therefore a greater degree of energy limitation, a smaller microbial population, and physical isolation between microbial decomposers and organic matter, contributing to slower turnover times with increasing depth (Fontaine et al., 2007; Schmidt et al., 2011; Hicks Pries et al., 2018).

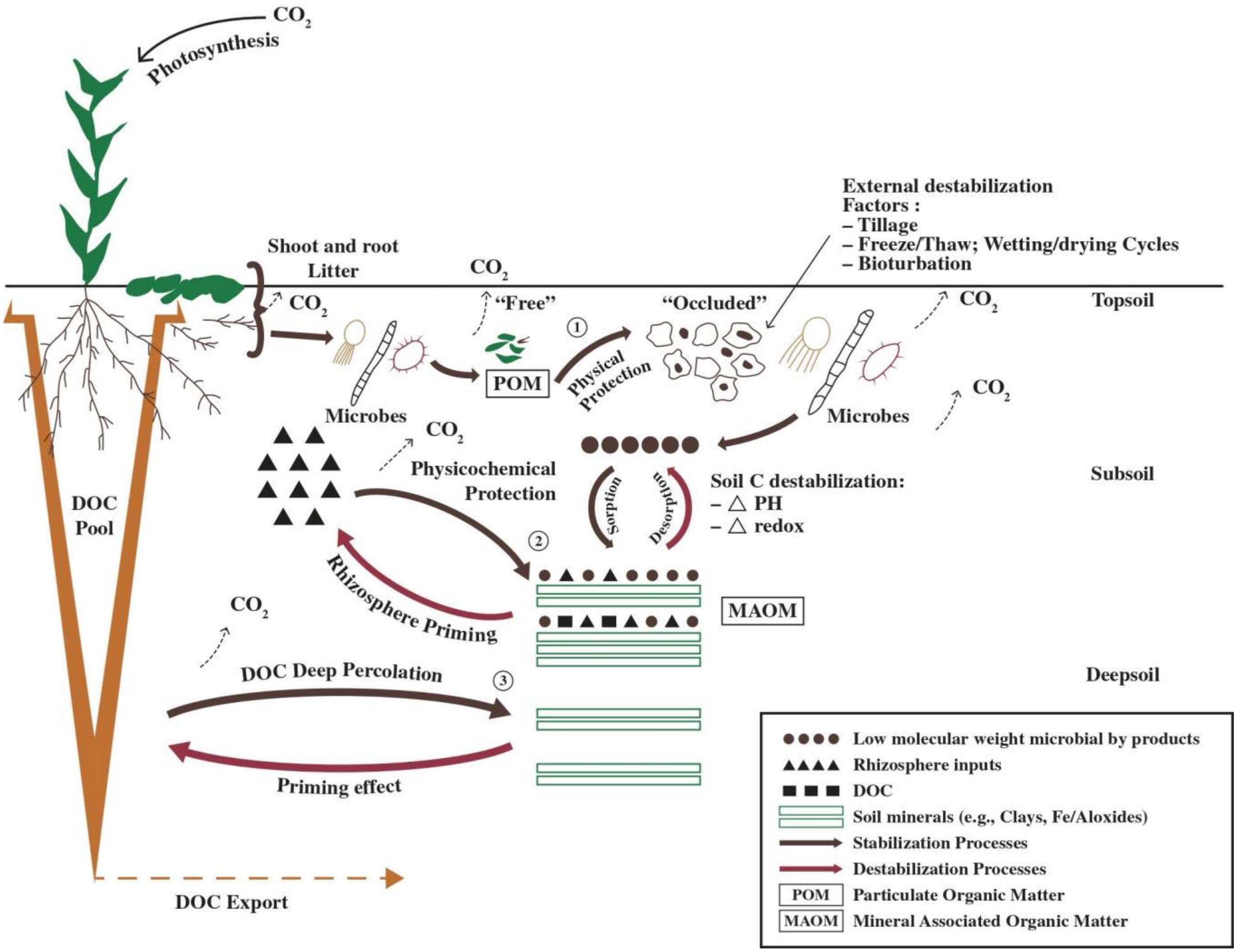

Figure 1.1 Summary of the main mechanisms of soil organic carbon stabilization/destabilization. (1) Physical protection, (2) Physicochemical protection, (3) DOC deep percolation.

Pedogenic processes and features of subsoils also contribute to C sequestration potentials, such as: (1) clay accumulation, a key characteristic of many subsoils, which promotes both higher MAOM saturation thresholds and stable microaggregate formation with the capacity to occlude POM (Six et al., 2000); (2) transformations of primary minerals and associated weathering products into secondary minerals within the subsoil, contributing to greater amounts of substrates to facilitate MAOM stabilization compared to topsoil (Rasmussen et al., 2006); and, (3) presence of large structural units, dense or cemented horizons typical of subsoils that can exclude roots, water, and air, limiting microbial activity and influencing physical transport mechanisms that further isolate SOC from bulk soil microbial communities (Schmidt et al., 2011).

Traditionally, deep SOC has been considered more stable (Harrison et al., 2011; Schmidt et al., 2011) and is also generally of older age (Liebmann et al., 2020). For instance, deep SOC storage at a 6-meter depth was recently found to persist for over 20,000 years (Moreland et al., 2021). However, while subsurface SOC stabilization and storage appears to occur relatively slowly (Liebmann et al., 2020), some lines of evidence suggest that deep SOC, mainly MAOM, may be proportionally more susceptible to rapid destabilization and decomposition than SOC in topsoil. This is due to changes in environmental conditions, such as soil properties and climate, as well as soil management practices (Harrison et al., 2011; Keiluweit et al., 2015; Shahzad et al., 2019). These conditions may affect the mineral surface charge and the mineral solubility, which will eventually lead to more soil organic carbon destabilization within the MAOM pool (Bailey et al., 2019).

For instance, soil pH and redox directly influence MAOM destabilization (Bailey et al., 2019; Rasmussen et al., 2018). A change in soil pH (increase or decrease) may induce a change in the mineral surface charge (positive or negative) (Bailey et al., 2019), and therefore its reactivity vis a vis the adsorption of certain SOC compounds (Bailey et al., 2019). Poorly crystalline iron oxides are among the soil minerals that are highly correlated with SOC content (Huang et al., 2016), and these colloids are susceptible to changes in redox potential (Bailey et al., 2019).

The significant input of fresh C is another factor that appears to accelerate destabilization of older SOM at greater depths via microbial priming (Jobbágy and Jackson, 2000; Fontaine et al., 2007), especially when introduced infrequently as a large quantity pulse input (Sokol et al., 2019). This may result during the mixing of large quantities of fresh POM or during a burst DOM flux from surface to sub-surface soil layers (e.g., caused by termination and/or incorporation of CC residues) (Nieminen, 2004; Evans et al., 2007; Fontaine et al., 2007; Butman et al., 2015). This may also occur due to the growth of deep rooting plant species, resulting from the production of several types of rhizodeposits (e.g., oxalic acid) that are shown to accelerate rhizosphere priming, and also the subsequent turnover of those roots during senescence (Keiluweit et al., 2015; Poirier et al., 2018). To this point, a recent experiment found that mixing living root inputs (rhizodeposits) with root litter inputs induced a loss of about 30% of MAOM through the rhizosphere priming effect (Sokol et al., 2019). Though temperature fluctuations are greatest near the soil surface, increasing temperatures are considered an additional exacerbating factor for increasing microbial priming rates of both surface and sub-surface SOC. Despite the relatively long turnover periods of deep SOM, a recent soil warming experiment indicated that SOC from the deeper profile could currently account for 25% of soil respiration (Hicks Pries et al., 2018), with substantial losses of soil C predicted under climate warming (Soong et al., 2021).

Alternatively, DOM is also a potential source of stabilized SOC in deeper soil horizons (Kalbitz and Kaiser, 2008; Rumpel and Kögel-Knabner, 2011). As DOM percolates vertically into subsoils, through soil pores and preferential flow paths (e.g., soil cracks, earthworms cast, root channels), certain SOC compounds become preferentially sorbed to mineral surfaces (Gross and Harrison, 2019). The vast majority of sub-surface MAOM content is microbially-derived, and thus, plant-derived DOM substances will generally undergo multiple sequences of transformation, sorption, and desorption during the process of percolating down the soil profile

(Liebmann et al., 2020). The availability of N plays a central role in the formation of microbially-derived SOM products, especially the persistent SOC found with MAOM (Cotrufo et al., 2019). The stronger affinity of soil minerals to smaller, highly-oxidized, hydrophobic, and nitrogenous organic compounds is likely a dominant reason behind the preferential sorption of proteinaceous microbial residues versus less proteinaceous plant residue (Jardine et al., 1989; Kaiser and Zech, 1997; Gleixner et al., 2002; Guggenberger and Kaiser, 2003; Kiem and Kögel-Knabner, 2003; Knicker, 2004; Kleber et al., 2007; Kaiser and Kalbitz, 2012; Stockmann et al., 2013; Lehmann and Kleber, 2015). This highlights the key importance of SOC quality (i.e., composition) in long-term MAOM storage (Barré et al., 2018), which is particularly relevant at depths where rhizodeposits are a dominant source of microbial energy (Baumert et al., 2018) and pedogenic transformations are the greatest (Kramer et al., 2017).

Carbon input frequency (infrequent ‘pulse’ vs. frequent ‘drip’) and spatial distribution are particularly important considerations for SOM stabilization in subsoil (Sokol and Bradford, 2019). Continuous, low-volume inputs of living root rhizodeposits, deeper in the soil profile, may facilitate steady microbial processing and stabilization pathways. On the other hand, large and infrequent pulses of DOM (via precipitation or irrigation) and POM (via tillage and incorporation) may facilitate ‘boom and bust’ cycles for the microbial community – the formation of a temporarily enlarged microbial population, without subsequent energy inputs, that results in significant metabolic priming of resident SOC pools.

Mechanisms that promote POM destabilization are generally linked to aggregate disruption factors associated with increased soil disturbance, which tend to be more frequent near the soil surface (Six et al., 2000). While a potential increase in soil cultivation with the adoption of cover cropping is notable, it is not the only considerable disturbance factor affecting POM destabilization. For instance, the alternation of freeze and thaw cycles may induce a break-up of soil aggregate through the expansion of water (Bailey et al., 2019). Wetting and drying cycles may further lead to shrinking and swelling for some types of clay (2:1 clays), which can reshape soil aggregates and induce a loss of the POM (Hu et al., 2015; Rahman et al., 2018). Aggregate disruption may also occur through SOC cycling by soil fauna or during a process known as bioturbation – the physical displacement of materials by soil fauna throughout the soil profile – which can induce either SOC destabilization or stabilization depending on the bioturbation agents and mode of action (Bailey et al., 2019). For instance, earthworms may cause destabilization through consumption and decomposition of SOC (Bailey et al., 2019). Yet, they may also act as stabilization agents through the mucilage they excrete, which favors the formation of microaggregates (Six et al., 2004, Bottinelli et al., 2015) and therefore increases SOC stabilization via physical occlusion within soil aggregates.

1.5 Differential SOC stabilization of above- and belowground biomass

Historically, the quantity and quality of the aboveground plant biomass fraction was considered as the overwhelmingly dominant driver determining SOC stocks (Larson et al., 1972; Rasmussen et al., 1980). Litter quality remains widely accepted as a major factor affecting SOM stabilization (Castellano et al., 2015), particularly at depth (Kramer et al., 2017). In order to link litter quality and SOC stabilization, Cotrufo et al. (2013) developed the Microbial Efficiency-Matrix Stabilization (MEMS) framework where plant litter that produces more microbial residues will likely result in more MAOM (Castellano et al., 2015). However, the ability to render a positive effect of new residue inputs within the MAOM pool is influenced by SOC saturation status (Castellano et al., 2015). In this model, improved litter quality will likely increase MAOM and result in a low saturation deficit (potential C sequestration) (Castellano et al., 2015). After saturation, litter quality wouldn't affect the storage of carbon within MAOM as much, the transfer of POM into MAOM would decrease (Castellano et al., 2015), and MAOM would be more prone to destabilization through SOC desorption mechanisms (Figure 1.1) (Bailey et al., 2019).

Recent studies provide more fine-grained and robust evidence suggesting that the belowground plant biomass fraction contributes more efficiently to stable SOC than aboveground carbon inputs, especially the MAOM pool (Poeplau and Don, 2015; Austin et al., 2017; Jackson et al., 2017; Poirier et al., 2018; Gross and Harrison, 2019; Sokol and Bradford, 2019). In fact, one study observed that the conversion efficiency of belowground vs. aboveground plant inputs toward SOM stabilization is as much as fivefold (Jackson et al., 2017). This aligns with another study, which found that the belowground fraction of cover crop inputs were three times more likely to remain as SOC in the 5 months after cover crop termination (Austin et al., 2017). This belowground input efficiency during the formation of stable SOM is assumed to result from a combination of (1) the relatively higher lability of belowground inputs, (2) close proximity and physical accessibility of belowground inputs to both the rhizosphere microbial community and soil mineral surfaces, and (3) higher deposition frequency of belowground inputs into the rhizosphere (Farrar et al., 2003; Rasse et al., 2005; Jackson et al., 2017; Sokol and Bradford, 2019).

The belowground plant fraction is composed of both root litter (e.g., root hairs, root debris) and living root inputs, rhizodeposition, (e.g., root exudates, secretions) (Rasse et al., 2005; Oburger and Jones, 2018).Rhizodeposition is diverse and dynamic in composition and can be either water-soluble -- such as sugars, amino acids, and organic acids -- or water-insoluble -- such as cell wall components, lipids, and mucilage (Canarini et al., 2019). Belowground organic carbon deposits are stabilized through different mechanisms depending on the origin of the input (Poirier et al., 2018). Root functional traits that are associated with storing POM are generally those that favor soil aggregation, which in turn limit the accessibility of occluded SOC to decomposers (von Lützow et al., 2008). Root litter, composed of structural materials such as cellulose and hemicellulose, are predominately stabilized through incorporation within soil aggregates (occluded POM) (Hättenschwiler and Vitousek, 2000; Rasse et al., 2005). Polyphenols and polysaccharides, produced by root mucilage, play an important role as a binding agent in soil aggregate synthesis (Oades, 1984; Martens, 2002), as does fungal hyphae both from symbiotic root-associations with mycorrhizal fungi (Wilson et al., 2009) and fungi that preferentially utilize rhizodeposits (Baumert et al., 2018).

On the other hand, root chemical characteristics such as higher root N and suberin content, and rhizodeposition of low molecular weight organic compounds, can promote SOC stabilization through interactions with soil minerals, thus forming MAOM (Rasse et al., 2005; Cotrufo et al., 2013, 2015; Austin et al., 2017). Soluble rhizodeposits such as exudated sugars and organic acids have direct stabilization pathways through sorption to mineral surfaces (MAOM) (Figure 1.1) (Kraffczyk et al., 1984; Austin et al., 2017; Liang et al., 2017; Sokol et al., 2019) so much so that they may not even require microbial processing beforehand (Mikutta et al., 2019; Angst et al., 2021). Notably, these soluble rhizodeposition may be the most efficient and effective mode of SOC stabilization, especially in subsoils where SOC content is below mineral saturation thresholds (Rasse et al., 2005; Austin et al., 2017). Even where mineral saturation is near thresholds, rhizodeposition is also essential in aggregate synthesis and SOC occlusion. To that point, one study observed living root rhizodeposition to be 2 to 13 times more efficient than litter inputs (above- and belowground) in contributing to both MAOM and POM accrual -- and much of the rhizodeposition was persistent up to 3 years later (Sokol et al., 2019). The efficiency of forming MAOM and POM from the belowground inputs (roots and rhizodeposition) is notably different, where rhizodeposition inputs have the highest MAOM efficiency compared to roots and shoots, and root litter has the highest POM formation efficiency (Villarino et al., 2021). The high efficiency of the belowground fraction in storing and stabilizing SOC, as well as the complementary role between rhizodeposition inputs and roots in forming MAOM and POM respectively, is useful information that can help advise novel cover crop management practices to capitalize on the role of the belowground fraction for increasing SOC sequestration in Mediterranean croplands.

1.6 Implications for cover crop management practices in Mediterranean regions

Harnessing the potential of cover crops to increase SOC sequestration will require strategic implementation of management considerations related to net primary productivity, fertility, plant community composition, termination method and residue management, and soil disturbance regime. Ultimately, the SOC sequestration potential of cover cropping will be determined by cumulative effects of climate and management on organic input quantity and quality, input and output flux rates, and the spatial distribution of deposits within the soil profile. Soil management practices also induces shifts in the physical habitat and resource availability of microbial communities and therefore CUE (Six et al., 2006). Here we consider cover crop selection and management approaches that could increase the efficacy of cover cropping in Mediterranean croplands for C sequestration (Table 1.1).

1.6.1 Species selection

Current understanding of SOC fluxes and sequestration mechanisms highlights the key role of belowground structure and soluble plant inputs in regulating soil and microbial processes associated with long term SOC storage. Strategic integration of cover crop functional groups has been shown to partially regulate SOC storage potential. Since a broad range of species can be cultivated as cover crops in Mediterranean agroecosystems, informing species selection and community assembly with the specific root functional traits shown to increase SOC and stabilization potential offers new opportunities to optimize management for long-term C storage (Poirier et al., 2018)

Plant growth strategies and root traits have significant legacy effects on soil C storage through nutrient uptake dynamics, quantity and quality of organic inputs and shaping of active microbial communities through exudation (De Deyn et al., 2008; Cantarel et al., 2015; Guyonnet et al., 2018). Frameworks examining linkages between root functional traits and C storage pathways have shown that root tissue chemical recalcitrance promotes MAOM formation while morphological traits seldom relate to stabilization mechanisms, except for rooting depth which is an important trait controlling root-C storage and stability in the subsoil (Poirier et al., 2018). Developing cover crop systems with high root depth distribution results in greater contact between root tissues and mineral surfaces in deeper soil layers and favor stable MAOM associations on less saturated mineral surfaces (Kell, 2011). Diverse species mixtures are increasingly favored to increase the array of beneficial functions one can obtain from cover crops. A positive relationship between plant diversity and SOC sequestration (De Deyn et al., 2008; Fornara and Tilman, 2008; Cong et al., 2014) has been demonstrated, especially in extensively managed systems.

Growing deep-rooted species with species that colonize complementary spatial-temporal niches could favor formation of both MAOM at depth and POM in the topsoil through a greater diversity of root traits, impacts on soil structure and spatial and temporal C inputs to soil ecosystems (Cong et al., 2014; DuPont et al., 2014; Lange et al., 2015; Kravchenko et al., 2019). For instance, species differently impact structural stability of soil particles important for POM storage. Whereas deep rooted species with coarse roots can increase soil bulk density adjacent to the root, smaller diameter roots can decrease bulk density by increasing soil porosity (Gyssels et al., 2005). Species with denser, finer root systems such as grasses bind soil more effectively than do large taproot systems (Loades et al., 2010), leading to greater macro aggregation in topsoil and accumulation of labile SOC in both macro and micro aggregates (Angers and Caron, 1998). Mixtures of grasses and legumes may be particularly effective and could include species with functional traits attributed to acquisitive strategies such as combining deep-rooted legume species (i.e., alfalfa (Medicago sativa) and faba beans (Vicia faba) with commonly managed grass species with extensive shallower fibrous root structures. Deeply rooted C4 grasses and shallow rooted legumes are also highly complementary functional groups with high C storage potential (Fornara and Tilman, 2008).

Prioritizing species mixtures could also be beneficial to enhance the amount and diversity of labile C inputs and microbial populations instrumental in building both POC and MAOM fractions (Lange et al., 2015; Tiemann et al., 2015). The amount and composition of root C efflux via root respiration, exudation and rhizodeposition vary among plant species (Bais et al., 2006; Herz et al., 2018; Dietz et al., 2020; Henneron et al., 2020) and it is likely possible to manipulate the abundance and composition of root exudates by modifying species composition. In general, in an agricultural context, choosing acquisitive growth types according to plant economic spectrum might be more suitable and effective for SOC storage than slow growing conservative species, since the higher photosynthesis and nutrient demand of acquisitive species triggers greater rhizodeposition (Henneron et al., 2020). However, our understanding of exudation patterns and quality in agricultural systems is very limited and a major knowledge gap in designing plant covers that harness this potential for long term SOC storage. Plants species that release more exudates will probably enhance their impact on aggregation and SOC occlusion pathways, along with species that exude larger molecules that can act as binding agents (Whalley et al., 2005). Root exudates from legumes are of particular interest since they have high concentrations of N-rich compounds compared to other species (Fustec et al., 2010) which can be rapidly assimilated in microbial biomass, increasing microbial CUE and MAOM content (de Neergaard and Gorissen, 2004; Cotrufo et al., 2013; Kopittke et al., 2020). Legumes ability to provide adequate N requirements for maximizing C storage often leads to greater SOC contents and accumulation of SOC is frequently observed across contexts and in macroaggregate shortly after legume growth (Topps et al., 2021). Legumes in cover crop mixtures with grasses are often found beneficial to cover crop productivity and C input from biomass (Fornara and Tilman, 2008; Freund et al., 2021).

Favoring species with beneficial biotic root traits can also impact SOC quantity and persistence through association with differing rhizosphere communities and mycorrhizal fungi (Langley et al., 2006; Averill et al., 2014). For instance, plants in symbiosis with ectomycorrhizal fungi, which lower decomposer activity by outcompeting them for N, store largely more SOC than arbuscular mycorrhizal associated plants. It has also been proposed that species with root traits that stimulate the growth of fungi over bacteria, such as high lignin and low root N content can promote SOC sequestration (De Deyn et al., 2008; Bardgett et al., 2013; Poirier et al., 2018).

This view is consistent with recent knowledge that fungal structures reside longer in soil whereas bacterial membranes are more quickly mineralized (Domeignoz-Horta et al., 2021). As such, bacteria-only communities can lead to more unstable and labile SOC pools compared to communities with bacteria and fungi (Domeignoz-Horta et al., 2021). Rhizobia in legumes can also promote aggregate formation and stability through the binding action of rhizobia exocellular polysaccharides (Haynes and Beare, 1997; Alami et al., 2000).

Research in extensively managed grassland systems shows that more diverse plant covers lead to more rapid annual carbon accumulation rates compared to monocultures thanks to greater above and belowground C inputs and soil N mineralization which fuel the soil microbial pump and prime positive diversity–productivity relationship (Cong et al., 2014; Yang et al., 2019;). Promoting a diverse array of C inputs through diversifying crop rotations with cover crops and adopting diverse cover crop species mixtures likely provide various resources that better optimize CUE (Kallenbach et al., 2019). In mild Mediterranean climates, extending the growth period of active living roots and inputs of C into the soil through cover cropping will also increase the period where microbial communities remain active. Mitigating long microbial dormancy periods may improve CUE over time (Kallenbach et al., 2019). Either way, maintaining more prolonged periods of metabolic activity annually, even with lower CUE, would presumably result in more microbially-derived C (necromass) than management strategies that facilitate low C inputs, high loss pathways, and longer periods of microbial dormancy, which may be typical of conventional systems (Kallenbach et al., 2019).

However, linkages between cover crop diversity, species choice and SOC outcomes remain to be tested in Mediterranean agroecosystems. Root functional frameworks and characterization of common cover crop species can inform cover crop management (Tribouillois et al., 2015; Wang et al., 2021) but outcomes remain context specific, especially when considering plastic root traits which vary considerably within species in response to resource gradients and ecological interactions. Cover crop species choice is also a function of other system management goals that must be reconciled with desired C storage outcomes. For instance, planting leguminous crops is preferred to maintain or increase soil N content (Ordóñez-Fernández et al., 2018), while other cover crop types such as grasses and brassicas might be useful for scavenging nutrients, increasing biomass inputs, and reducing N leaching. Finally, modifications of soil properties regulating SOC storage, including microbial communities, are strongly linked to cover crop management and edaphic properties, in some cases more so than species choice and diversity (Romdhane et al., 2019; Cloutier et al., 2020).

1.6.2 Cover crop growth phase and planting duration

Adjusting cover crop growth duration by selecting cover crop planting and termination times is an intrinsic consideration when managing cover crops (Alonso-Ayuso et al., 2014), especially in Mediterranean agroecosystems which may facilitate a wide range of growth periods. For the objective of increasing SOC sequestration, cover crop growth duration is the most important predictor of SOC responses to cover cropping, as was recently highlighted in a meta-analysis study (McClelland et al., 2021). This importance is likely due to interactions between the cover crop growth period and other factors like plant establishment, plant biomass (McClelland et al., 2021) and residue quality (Clark et al., 1994; Alonso-Ayuso et al., 2014).

Organic C preservation depends on the balance between SOC stabilization and destabilization mechanisms (Janzen, 2006; Harden et al., 2018; Bailey et al., 2019), and litter quality affects the balance between these two mechanisms (Bailey et al., 2019). For example, high quality residues characterized by low C:N ratios or the predominance of simple compounds, have a high microbial CUE (Cotrufo et al., 2013), where the resulting microbial by-products can be efficiently stabilized within the MAOM pool (Six et al., 2002; von Lützow et al., 2007;

Cotrufo et al., 2013). These same labile products can act as destabilizing agents via the priming effect (Jobbágy and Jackson, 2000; Fontaine et al., 2007; Bailey et al., 2019). Therefore, we propose that adjusting cover crop growth duration as a function of litter quality and SOC saturation status could contribute towards balancing stabilization and destabilization mechanisms, hence optimizing SOC sequestration through proper cover crop management. Cover crop termination at early stages of plant development may result in higher plant litter quality that is more easily assimilated by microbes. As a result, the increased microbial necromass is likely to favor MAOM stabilization mechanisms. After MAOM saturation, further accrual of SOC will shift to POM stabilization mechanisms. Thus, at this stage, cover crop management practices that favor promotion of aggregation will become the dominant pathway for continued SOC sequestration. However, more studies are needed to effectively assess cover crop termination time with regards to SOC stabilization and destabilization mechanisms across contexts. In particular, the impacts of soil fertility on plant growth and optimal termination for SOC accrual remain elusive, yet critical to promote plant allocation of carbon to preferential storage flows, especially belowground.

Recent literature suggests that conditions that repress aboveground growth, while still allowing photosynthesis to continue, facilitates the allocation of surplus photosynthates toward exudation and root structures (Prescott et al., 2020). This is especially relevant when considering strategic nitrogen (N) management. For instance, the beneficial effects of N availability for MAOM formation may be counteracted as N fertilizers also reduce biomass allocation toward roots and therefore decrease belowground C deposition (Bonifas et al., 2005; Lazicki et al., 2016; Pausch and Kuzyakov, 2018;(Ordóñez et al., 2021), the quantity of exudates produced (Kaštovská et al., 2017; Mortensen et al., 2021), and plant C flux rates toward soil communities

(Gorka et al., 2019). Another strategic consideration is that the release of exudates appears to be maximized in leguminous species when phosphorous (P) is limited (Cardenas et al., 2021). Likewise, moderate drought can increase root exudation and rhizodeposition (Karlowsky et al., 2018). Managing cover crop growth conditions to favor photosynthate transport belowground in consideration of root growth, exudation, and the spatial hotspots of microbial activity (such as within the rhizosphere) may therefore be an important regulation factor to maximize SOC stabilization outcomes.

Alternatively, maintaining sufficient soil N availability over the long-term has been shown as essential toward increasing both MOAM and POM (Ordóñez et al., 2021; Rocci et al., 2021; Spohn, Pötsch, et al., 2016). This may be especially true when targeting increases in aboveground productivity and POM accumulation, such as when MOAM storage thresholds are near saturation (Rocci et al. 2021). Additionally, higher N fertility suppresses the breakdown of lignin in plant residues, which slows decompositional processes and may increase POM persistance (Li et al., 2017; Talbot & Treseder, 2012). Managing for optimal N fertility is essential toward improving microbial CUE and, therefore, the efficiency of SOC formation (Li et al., 2017; Mahal et al., 2019; Ordóñez et al., 2021). Optimizing SOC benefits of cover cropping will therefore require more precise nutrient management approaches that balance higher nutrient requirements of the crop, for optimizing aboveground productivity, with maintaining lower, yet sufficient, nutrient status during the cover crop phase to optimize belowground productivity and SOC sequestration. Deciding on the growth period of cover crops could be considered a potential management tool to optimize SOC preservation in croplands with Mediterranean climate, especially with respect to fertility management, the promotion of belowground productivity, and optimizing litter quality inputs. This decision is site-specific and depends on intrinsic soil characteristics, as well as external factors such as climate and other co-management variables. Hence, more research is needed in order to delineate easy-to-use indicators that would guide farmers' decisions to choose proper cover crop plantation and termination times.

1.6.1 Termination and residue management methodologies

The design and application of cover crop termination strategies are a readily accessible tool available for growers to optimize cover cropping for increased C sequestration. Modes of cover crop termination may be classified into three broad categories that include chemical (herbicides), mechanical, and natural methods. Mechanical termination methods have the broadest applications and include mowing, rolling/crimping, and a wide array of tillage options. Natural termination methods may include planting of winter-kill species (though not common in Mediterranean climates) and the use of animal grazing on residues. Cover crop residue management is an additional consideration and options may include retention on the soil surface, incorporation into soil profile, and/or biomass removal through grazing or harvesting. The various combinations of management choices have significant impacts on the quantity and quality of above- and belowground carbon deposition, as well as the spatial distribution dynamics of deposited organic and inorganic inputs. Linking cover crop management with SOC accumulation and persistence frameworks should guide our efforts to adapt cover crop termination methods with the objective of sequestering more carbon and ensuring its long-term storage.

A predominant determinant of cover cropping efficacy with respect to SOC sequestration is the choice to retain or incorporate residues upon termination. The choice to incorporate residues is done through the use of tillage, which may occur for several reasons including to mix organic and inorganic materials throughout the soil profile, mitigate weed pressure, and/or break apart soil surface compaction for improved planting and water infiltration (Derpsch, 2003; Derpsch et al., 2014). Yet, while tillage facilitates the incorporation of aboveground residue-derived POM throughout the soil profile (Duval et al., 2016; Schaefer et al., 2020), heavy tillage has also been shown to stimulate SOC losses through disrupting aggregate stability and increasing microbial access to previously occluded intra-aggregate POM (Franzluebbers et al., 1999, Six et al., 2000; Salvo et al., 2010; Poeplau and Don, 2015). Heavy tillage is also associated with significantly higher rates of SOC loss via surface erosion (Van Oost et al., 2006). To this extent, POM is actually most often lower in the surface soils of conventionally tilled systems, despite this increased incorporation of aboveground cover crop residues (Motta et al., 2007; Olchin et al., 2008; Franzluebbers and Stuedemann, 2014; Jilling et al., 2020;). Though more variable, the use of tillage is also sometimes associated with reductions in MAOM (Salvo et al., 2010; Jilling et al., 2020). These factors therefore contribute to a well-established negative relationship between conventional tillage and total SOC stocks of surface soils when compared to no-till and conservation tillage strategies, particularly within the tillage zone where significant disturbance occurs (Salvo et al., 2002; Hobbs et al., 2008; Salvo et al., 2010; Franzluebbers and Stuedemann, 2014; Higashi et al., 2014; Poeplau and Don, 2015; Nunes et al., 2020; McClelland et al., 2021; Wulanningtyas et al., 2021). Notably, our understanding of tillage dynamics is limited by the tendency to discuss the various types of conversation tillage, and their underlying impacts, as a monolith rather than as a dynamic tool that differs in application and subsequent SOC dynamics (Derpsch et al., 2014).

To this extent, the impacts of various tillage regimes on sub-surface SOC storage are a current point of controversy. A growing body of evidence has observed decreased SOC stocks in subsoils with the conversion from conventional tillage to no-till management of cover crops

(Franzluebbers and Stuedemann, 2014; Camarotto et al., 2020). While the underlying mechanisms are not yet well understood, this decrease in deeper SOC sequestration during the transition toward no-till may result from reductions in cover crop establishment and subsequent decreases in above- and belowground biomass production (Constantin et al., 2010; Camarotto et al., 2020;). This may potentially be remediated by some conservation tillage methods (Franzluebbers et al., 1999; Jilling et al., 2020), increasing cover crop seeding rates, and/or extending the cover crop cultivation window. Further, it may also be that the negative subsoil SOC response with the conversion to no-till results partially from increases in SOC priming, which may be especially prevalent within conventionally managed systems with significant soluble N inputs (Duval et al., 2016; Tautges et al., 2019; Camarotto et al., 2020). Some research suggests that this same priming response may be mitigated when organic inputs, such as compost, are paired with cover cropping in both tilled and no-till systems (Fronning et al., 2008; Liang et al., 2018; Tautges et al., 2019; Schaefer et al., 2020; White et al., 2020; Rath et al., 2021).

Though significantly understudied in agricultural systems, residue incorporation may also occur through bioturbation and the physical transport of materials deeper into the soil profile (Lavelle et al., 2006; Frouz et al., 2009). While the negative impacts of tillage on soil fauna populations are well documented (House and Parmelee, 1985; Emmerling, 2001), less is understood on how this directly impacts the transport dynamics of SOC throughout agroecosystem soils. Nevertheless, retention of surface residues has been shown as essential to the prosperity of soil fauna communities (Tian et al., 1995; Lavelle et al., 2006, 2016), and research has increasingly shown the role these organisms may play in SOC cycling within natural ecosystems (Filser et al., 2016). While further research is necessary, this may partially explain why POM stocks are often found to be higher in surface soils under no-till with residue retention strategies when compared to residue incorporation via tillage. Notably, there is scarce research conducted on the impacts of lower frequency tillage events. Thus, our understanding of the benefits and/or tradeoffs associated with the infrequent use of tillage in more temporally dynamic cover crop termination rotations are not well understood. Ultimately, keeping cover crop residues on-field, whether through promoting residue retention on the soil surface or through incorporation, has been shown as essential to improving SOC storage (Kan et al., 2020; Wang et al., 2020; Zhao et al., 2020).

Yet, residue surface retention strategies, such as herbicides, mowing, and roller-crimping, have shown a wide array of benefits associated with the ‘soil armor’ effect of reducing bare soil exposure. This includes increases in SOC (Turmel et al., 2015; Chen et al., 2017; Alam et al., 2018; Li et al., 2019; Sharma et al., 2019; Wang et al., 2019; Zhao et al., 2020) and soil structure (Chen et al., 2017; Li et al., 2019; Wang et al., 2019) that, in tandem with the insulating effect of residue layers, improves the regulation of soil temperature (Schonbeck and Evanylo, 1998; Sarkar and Singh, 2007) and retention of soil water (Schonbeck and Evanylo, 1998; Sarkar and Singh, 2007; Turmel et al., 2015; Yin et al., 2020; Zhao et al., 2020). Some studies have shown a decrease in soil carbon priming with the interaction of no-till and residue retention strategies when compared to residue incorporation (Kan et al., 2020; Mo et al., 2021). Residue incorporation may, in fact, only further increase SOC priming as the quantity of biomass incorporated increases (Shahbaz et al., 2017; Shahbaz et al., 2017a). However, little is known about the varying relative impacts of chopping (via mowing) and matting (via roller-crimping) of cover crop residues. The relative effects of evenly distributing or spatially concentrating residues are also not well understood. Residue retention strategies vary widely in application, both in time and space. Yet, the spatial and temporal diversity of these strategies are not captured well in research, and instead are often conflated and inaccurately represented as a single management practice rather a suite of management options. Thus, the best management practices are not yet well identified in Mediterranean climates.

Depending on the cover crop composition, one of the drawbacks associated with surface residue retention is potential reductions in available N (Hefner et al., 2020; Jani et al., 2019; Ordóñez-Fernández et al., 2018). This may both reduce crop productivity (Hefner et al., 2020) and stoichiometrically limit stable SOC formation (Bertrand et al., 2019), though these outcomes are likely highly dependent on residue nutrient content and carbon quality (Bertrand et al., 2019; Mo et al., 2021) and, as previously mentioned, may be a strategic benefit for SOC stabilization in cropland soils with high N application rates. Where N availability places stoichiometric limitations, this may potentially be addressed through increasing the planting of leguminous species thereby improving the N content and mineralization rates of surface retained residues (Büchi et al., 2018; De Notaris et al., 2020). The CUE of cover crop residues may also be increased through the strategic application of nutrients, whether during the cash crop or cover crop phase, to help balance stoichiometric needs between C and other essential nutrients that may limit microbial assimilation and anabolism of C substrates.

Another option may be the strategic introduction of animal grazing into cover cropping rotations. While grazing animals on cropland, especially as a cover crop termination method, is fairly understudied, there is some validation that well-managed cropland grazing may increase soil C sequestration (Franzluebbers and Stuedemann, 2010; Fultz et al., 2013; Assmann et al., 2014; Cecagno et al., 2018; Bieluczyk et al., 2020; Brewer and Gaudin, 2020; Liebig et al., 2020; Sekaran et al., 2021; Zani et al., 2021). Animal grazing of cover crops alters carbon and nutrient input flows into the soil through the transformation of aboveground residues into soluble, nutrient-rich, and labile animal excreta, where the DOC and nutrients are stoichiometrically decoupled and more easily diffused and transported throughout the soil profile (Carvalho et al., 2010; Ramos et al., 2010; Rumpel and Kögel-Knabner, 2011; Rumpel et al., 2015; Eldridge et al., 2017; Sekaran et al., 2021). Soil carbon and nutrient inputs from grazing may therefore be both more readily available for plant uptake (Holford, 1980; Lemaire et al., 2014; Zhou et al., 2017) and easily transformed by soil microbes (Acosta-Martínez et al., 2004; Wilson et al., 2018; Sekaran et al., 2021), potentially facilitating a more direct pathway toward long-term MAOM stabilization and persistence (Cotrufo et al., 2013; Mosier et al., 2021) However, differences in MAOM are often insignificant between grazed and ungrazed cropland (Salvo et al., 2010; Assmann et al., 2014; Zani et al., 2021) and long-term grazing can reduce total soil N content over time through export within animal biomass.

Grazing, especially when conducted multiple times throughout the cover crop growing season, may also result in both changes in cover crop biomass productivity and a reallocation of resources above- and belowground (Dawson et al., 2000; Hamilton et al., 2008; Zhou et al., 2017). Multiple studies have shown an increase in cover crop root biomass (Piñeiro et al., 2010; Assmann et al., 2014; Chen et al., 2015) and rhizodeposition of labile carbon (Dawson et al., 2000; Wilson et al., 2018) with the introduction of grazing. The magnitude and direction of SOC impacts will be determined by the frequency and intensity (density and duration) under which grazing occurs. Low intensity stocking rates and/or less frequent grazing events have broadly shown positive results for SOC sequestration (Conant et al., 2003; Teague et al., 2011; Assmann et al., 2014; Chen et al., 2015; Zhou et al., 2017; Alves et al., 2020; Mosier et al., 2021). Thus, optimizing best management practices for cover crop grazing will require strategic consideration of site-specific thresholds at which high intensity grazing becomes negatively associated with SOC storage (Teague et al., 2011; McSherry and Ritchie, 2013; Chen et al., 2015; Plaza-Bonilla et al., 2015).

In the final analysis, cover crop termination and residue management schemes may best be designed in a way to avoid prescriptive implementation -- utilizing the same regime year-after-year regardless of changes in climatic, ecological, and soil biogeochemical characteristics -- and instead applied strategically in a way to adapt to these same changes over time. As such, a strategic and temporally dynamic termination rotation of residue retention (via mowing, herbicides, or roller-crimping), residue incorporation (via conservation tillage), and residue grazing practices may yield the best results for cover crop management with respect to increasing SOC sequestration. This may be guided by the simultaneous goals of maintaining continuous inputs of shoot and root-derived C, diversifying the spatial and temporal input of shoot-derived C, reducing soil disturbance, and improving soil microbial efficiency through balancing the C-to-nutrient stoichiometric demands of SOC formation processes (Ferreira et al., 2018; Bertrand et al., 2019).

Table 1.1 Summary table of considerations for cover crop management to promote soil organic carbon sequestration

<table>
<tr><th colspan="2">Suggested considerations of cover crop management strategies</th></tr>
<tr><th>*Before* soil MAOM saturation</th><th>*After* soil MAOM saturation</th></tr>
<tr><td>Main objective:
Target soil C increases in both SOC fractions, POM and MAOM</td><td>Main objective:
Target soil C inputs as POM and avoid practices that cause MAOM destabilization</td></tr>
<tr><td colspan="2">Species selection</td></tr>
<tr><td>• Prioritize mixtures with a variety of complementary acquisitive growth strategies which triggers greater rhizodeposition and encourages large C pulses into the soil matrix.
• Plant cover crop species with a deep rooting system to promote rhizodeposition in deep soil horizons where colloids are more likely to be unsaturated with SOC.
• Mix leguminous cover crops with other species to optimize residue quality and enhance microbial CUE.</td><td>• Prioritize mixtures with conservative species.
• Avoid priming of subsoil MAOM by selecting shallow rooting cover crop species with lower rhizosphere inputs, such as those with coarser roots.
• Promote physical protection of POM by selecting cover crops with extensive shallow fibrous roots with higher root density (e.g., grasses) to enhance aggregation.
• Promote association with mycorrhizal fungi. Fungal products such as proteins favor soil particle aggregation, facilitating more POM physical protection</td></tr>
<tr><td colspan="2">Cover crop growth phase and planting duration</td></tr>
<tr><td>• Terminate cover crops earlier to promote high quality litter inputs with greater microbial CUE during decomposition.
• Tightly control nutrient budgets to limit N and P availability during cover crop growth phase (promote root formation and allocation of surplus photosynthates toward exudation) and increase N and P availability during cash crop growth phase (improve microbial CUE during decomposition)</td><td>• Terminate cover crop later to promote formation of low-quality (high C:N) inputs, with more plant structural compounds that form POM.
• Tightly control nutrient budgets to increase N availability during both cover crop and cash crop growth phase (to improve aboveground productivity and slow residue decomposition)</td></tr>
</table>

Termination and residue management methodologies	
● Infrequent conservation tillage, especially when paired with external organic inputs, may favor storage within MAOM (reduce SOC priming) compared to no-till, especially in deeper subsoils. ● Reduce bare soil exposure by increasing soil surface residue retention (through mowing, roller-crimping, or herbicides) ● Grazing* at low intensity increases dissolved C and N inputs. This enhances microbial biomass and activity, which may lead to MAOM increases	● Infrequent conservation tillage to reduce aggregate breakdown and microbial accessibility to occluded POM. ● Reduce bare soil exposure by increasing soil surface residue retention (through mowing, roller-crimping, or herbicides) ● Maintain slower aboveground residue input rates by avoiding excessive biomass incorporation (reduce SOC priming)

* Other parameters related to grazing that need to be taken into consideration, such as grazing intensity, frequency, and duration.

1.7 Conclusion

We considered cover crop selection and management approaches that could increase the effectiveness of cover cropping in the Mediterranean croplands for C sequestration following three main guiding principles (Table 1.1). However, significant gaps remain in understanding best management practices for C accrual, especially in Mediterranean systems. We highlight the need for:

1) Clearer SOC measurements and monitoring in these systems to guide cover crop management efforts towards targeting increases in both POM and MAOM fractions (when under mineral C saturation thresholds), or maintaining MAOM content while increasing the POM fraction (when at mineral C saturation thresholds);
2) Specifically outlining the determining root functional traits associated with SOC storage in both POM and MAOM fractions and identify cover crop species with greater contributions from belowground fractions.

3) Synthesis of depth dependent SOC stabilization and destabilization mechanisms in the MAOM fraction, and interpretation and application of cover crop management strategies that may shift the equilibrium between these two processes toward net stabilization.

Considering the evolution of SOC sequestration theory, we see opportunities for growers to implement new cover crop management strategies that capitalize on this knowledge. In-turn, as these strategies become standard, more systematic evaluations in field settings across soils and systems in Mediterranean climates will occur and advance our understanding of agriculturally managed SOC sequestration.

1.8 References

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Chapter 2 Estimation of Phosphorus sorption capacity for California soils based on routinely measured soil data.

2.1 Abstract

Documenting phosphorus sorption capacity (PSC) in soil is an essential step in effective nutrient management programs, but PSC is not routinely measured in most commercial laboratories. Pedotransfer functions could be used to estimate PSC. However, existing pedotransfer functions are developed using extractable Fe and Al, which is costly and not commonly measured. We aim to estimate Phosphorus Sorption Index (PSI) with widely available soil information using soil color parameters as proxies for pedogenic iron along with other commonly accessible soil data, notably, available P, clay, and organic carbon. A multiple linear regression model was built using soil redness *(a)*, soil yellowness *(b)*, Olsen P and organic carbon to predict PSI from a database of vinicultural soils in Napa County. The model performed reasonably when considering all soils including Entisols, Mollisols, Vertisols, Alfisols and Ultisols (R^2=0.62). The model fit increased (R^2= 0.72) when highly developed soils with very high PSI were removed. Results suggest there is great potential to leverage standard measurements from observations from the field or soil survey to guide regional patterns in P sorption and availability.

2.2 Introduction

Phosphorus (P) is one of the key macronutrients essential for maintaining high crop production (Liu et al., 2017); it is responsible for plant growth and development (Debicka et al., 2016) and plays a crucial role in phosphorylation and production of adenosine triphosphate, a major energy-carrying molecule (Fink et al., 2016a). P plays a major role in promoting root proliferation and soil organic carbon sequestration (Grant et al., 2020; Zeng & Wang, 2015; Zhao et al., 2017). P is one of the most reactive nutrients in soils with almost 80% of applied P susceptible to mechanisms of sorption or precipitation to unavailable forms (Gustafsson et al., 2012; Roberts & Johnston, 2015; Withers et al., 2001; Zhu et al., 2018). Depending on soil pH, P sorption can occur on Fe/Al (oxyhydr)oxide minerals, clay edges, and certain organic matter functional groups, or it may react with calcium and precipitate as calcium phosphate, rendering it less available for plant uptake (Lair et al., 2009). Furthermore, P is a non-renewable resource and will eventually decline (Cordell et al., 2009; Cordell & White, 2011), making the objective of ensuring food security for a constantly growing population even more challenging to achieve (Zhang et al., 2021).

The capacity of soil to retain P is limited, and once P sorption sites become saturated, the bonds between the adsorbents and P weaken (Borggaard et al., 2004). Thus, any additional P will remain in soil solution, increasing its susceptibility to losses via runoff, subsurface flow or leaching (Breeuwsma & Silva, 1992; Hughes et al., 2000; Borggaard et al., 2004; Wurtsbaugh et al., 2019). Subsurface losses predominate in soils with preferential flow pathways, such as coarse-textured soils and cracking clay soils (Radcliffe et al., 2015), and in cases where topsoil is P enriched, since any additional P may be more prone to leaching (Lookman et al., 1995; Del Campillo et al., 1999; Kleinman et al., 1999; Leinweber et al., 1999; Hooda et al., 2000). P discharge into surface water bodies constitutes a major environmental and public health threat (Walton, 2022). Furthermore, P losses will eventually increase as a result of the changing climate due to intense rainfall events and extended drought (Ockenden et al., 2017). Thus, assessing soil's capacity to retain P is crucial to devise sustainable P management strategies and reduce the associated environmental risks.

P sorption capacity (PSC) is an estimate of the soil's capacity to fix P. It provides insight into the threshold of legacy phosphorus levels, beyond which possible P losses through subsurface flow or leaching can occur (Welikhe et al., 2020), and is used to determine the optimum amount of fertilizer P to apply (Ciampitti et al., 2011; Y. t. Wang et al., 2015). Methods for quantifying PSC are essential for regional P management strategies. Similarly, P sorption index (PSI) provides estimates of effective P sorption capacity or remaining P sorption capacity (Kuo, 1988). While it has been shown that PSI demonstrates a strong and positive correlation with PSC (r=0.975) (Bache & Williams, 1971), testing for this parameter is not commonly performed in most commercial soil testing laboratories, and this type of information is not accessible to growers. Several pedotransfer functions aim to predict P related indicators such as PSC (Maguire et al., 2001; Borggaard et al., 2004; Borggaard et al., 2005b; H. Zhang et al., 2005; Welikhe et al., 2020), phosphorus sorption isotherm parameters (Dunne et al., 2021), and degree of phosphorus saturation (Kleinman et al., 1999; Kleinman & Sharpley, 2002; Renneson et al., 2015). These functions are based on pedogenic Fe and Al content in the soil and are tailored for more highly developed soils. Measurement of pedogenic Fe and Al is a costly and time-consuming analysis that is uncommon in commercial laboratories, and thus, may not be an effective parameter for estimating P fixation for the agricultural industry. Alternatively, soil color has been widely used to describe soil development and infer soil properties such as soil organic carbon, calcite, hematite, and goethite. Iron oxide minerals influence soil color parameters (Poppiel et al., 2020; Torrent et al., 1980, 1983). For instance, Torrent et al. (1983) showed that there is a close relationship between Fe oxides minerals (e.g., Hematite) and soil redness *(a)*, while others found a close relationship between the yellowness *(b)* of the soil and goethite minerals (Vodyanitskii & Kirillova, 2016).

Given the complexity of P cycling in soil, no cost-effective techniques exist to fully inform P management strategies. In order to foster a more comprehensive understanding of P in agricultural decision making, we tested the applicability of readily available soil parameters, such as soil color, pH, soil organic carbon and clay content to predict the maximum PSI at different soil depths, given that while the topsoil is highly influenced by human activities (e.g, fertilization, tillage), differences in subsoil are driven by factors and processes such as parent material, clay translocation and mineralogical transformations. The specific objectives of this study are to (1) identify a combination of easily measured soil parameters that would serve as effective proxies to estimate PSC in California vineyards; (2) Build a multiple linear regression model and assess its performance at different soil depths (topsoil, subsoil and deep soil) and for different soil types; and, (3) evaluate model fit among different soil taxa.

2.3 Material and Methods

2.3.1 Description of the study area

Soils were collected from 96 sites in 32 vineyards, with three sites per vineyard throughout the Napa Valley American Viticultural Area (AVA). This region offers a diversity of mesoclimates, soils, and topography (Burns et al., 2015). A stratified random sampling design was used to identify groups from Soil Survey Geographic Database (Burns et al., 2015). These groups reflected major differences in soil development, parent material and topography. Within each group, sites were identified and randomly sampled. The 32 vineyards comprise eight soil great groups: Haploxeralfs, Palexeralfs; Haploxerolls, Agrixerolls; Xerofluvents; Haplohumults, Haploxerults corresponding to four soil orders (Alfisols, Mollisols, Entisols, Ultisols).

2.3.2 Soil Sampling and physicochemical characterization

Soil samples were taken between May and July 2011 from three randomly chosen rows in each vineyard. At each of the three rows, three soil pits of approximately 50-cm diameter and

100-cm depth, spaced about 5-m apart, were excavated. Each soil pit was divided into five depths for characterization: 0 to 5, 5 to 10, 10 to 30, 30 to 50, and 50 to 100 cm.
About 500 g of soil was sampled from each depth of each soil pit and combined into a composite sample for physicochemical characterization. Air-dried, subsamples were sieved to pass 2 mm and analyzed for exchangeable calcium (Ca, mg/kg), particle size distribution (Percent Clay and Silt), pH, total organic carbon content (Percent C, g/g), available Olsen P (mg/kg), oxalate extractable iron (Fe-ox, mg/kg) (Burt, Rebecca & Soil Survey Staff, 2014) and citrate dithionite extractable iron (Holmgren, 1967) (Fe-cd, mg/kg). Oxalate extractable Fe (Fe-ox) originates from organic complexes and poorly crystalline Fe-oxyhydroxides (e.g., ferrihydrite). Citrate-dithionite extractable Fe (Fe-cd) originates from organic complexes poorly crystalline and crystalline Fe-oxyhydroxides. The crystalline iron was calculated as the difference between Fe-cd and Fe-ox (crystalline Fe= Fe-cd – Fe-ox).

Exchangeable cations were measured in 1M neutral NH_4-acetate extracts, particle size distribution was determined by the pipette method, total carbon using an ECS 4010 CHNSO Analyzer (Costech Analytical Technologies, CA, USA) (Burt, Rebecca, 2004). Given the relatively the low pH of these soils and high rainfall, total C can be considered organic C. Available P was determined based on the Olsen method (Olsen, 1954). Soil pH was determined after 30-min equilibration using a 1:1 soil water ratio.

Phosphorus sorption index was measured using a single-point sorption isotherm 75 mg PO_4-P/kg (Sims, 2009)

$$\mathrm{PSI} = \frac{x}{log(c)} \tag{1}$$

PSI is in L/kg where *x* represents the amount of added P adsorbed in the soil sample (mg/kg) and *c* is the P concentration (mg/L) in the filtered equilibrium solution.

2.3.3 Soil color measurement

Soil color parameters were measured using a Konica Minolta (CR-400) chromameter where air-dried, sieved (2 mm) soil samples were placed on a disposable sample cup and irradiated by an internal C65 standard light source. The sensor head was calibrated with a CR-A43 white calibration plate after approximately 10 measurements.

This system has three main parameters, (L), (a), and (b). The *(L)* parameter (lightness) is inversely correlated with dark pigment in soil (e.g., humus), where L values range from no reflection for black (L=0) to perfect diffuse reflection for white (L=100) (Torrent & Barrón, 1993). The *(a)* parameter (redness) is directly proportional to the content of red pigmented minerals (hematite), and the *(b)* parameter (yellowness) is directly proportional to the content of yellow pigmented mineral (goethite) (Kirillova et al., 2015).

A redness index (RI) was computed using the three color components *(L)*, *(a)*, and *(b)* based on the equation developed by Barron & Torrent (1986):

$$RI = \frac{\mathrm{a} * ((\mathrm{a})^2 + (\mathrm{b})^2)^{0.5} * 10^{10}}{\mathrm{b} * \mathrm{L}^6} \tag{2}$$

2.3.4 Data analysis

Data from horizons were pooled into three depth tiers topsoil (0-10 cm), subsoil (10-50 cm) and deep soil (50-100 cm). In order to assess the strength of the relationship between soil color parameters lightness (L), redness (a), yellowness (b), redness index and the variable forms of pedogenic iron (Fe-ox, Fe-cd, crystalline iron), we conducted a Spearman rank correlation as not all the data followed a normal distribution. Cohen's standard was used to evaluate the strength of the relationships, where correlation coefficients between 0.10 and 0.29 represent a small effect size, coefficients between 0.30 and 0.49 represent a moderate effect size, and coefficients above 0.50 indicate a large effect size (Cohen, 1988). In this study, variables that were statistically significant ($P\text{-value} < 0.05$) and had a correlation coefficient ($r > 0.50$) were considered to have a strong correlation.

A backward stepwise regression was performed to identify the set of explanatory variables that captured much of the variation in PSI at different soil depths. Several iterations were performed, where the selection criteria were based on variables that were statistically significant ($P\text{-value} <0.05$). A multiple linear regression model was built based on the selected predictors where root mean square error (RMSE) and coefficient of determination (R^2) were calculated to quantify the predictive performance of models that were built. All statistical analysis were performed using JMP® 16 Pro (SAS Institute Inc., Cary, NC, 1989-2023).

2.4 Results

2.4.1 Summary statistics

Soil characteristics summarized by depth intervals (topsoil, subsoil and deep soil) reflect variability from management and pedogenic processes (Table 2.1). Mean PSI increased with depth, but values were not significantly different due to high variability. PSI ranged from an average of 169 L/kg in topsoil (0-10 cm) to 201 L/kg in deep soil (50-100 cm). Similar trends were evident for soil pH, exchangeable calcium (Ca), different forms of Fe oxides and soil color, including lightness (L), redness (a) and redness index. In contrast, mean pH did not differ with soil depth. Topsoil (0-10 cm) was characterized by significantly higher Olsen P ($\bar{x} = 21.1$ mg/kg), silt content ($\bar{x}$ =41%) and soil organic carbon content ($\bar{x}$ =2.32 %). Deep soil (50-100 cm) was characterized by significantly higher clay content ($\bar{x}$ =22%) and a significantly higher yellowness color parameter (b).

Table 2.1 Summary statistics (mean ± standard deviation) of key physio-chemical soil characteristics by soil depth.

Soil depth	**N**	**Fe-cd (mg/kg)**	**Fe-ox (mg/kg)**	**Crystalline Fe (mg/kg)**
Topsoil	18	16561±8118 ^{a}	3346± 1264 ^{a}	13215 ± 7714^{a}
Subsoil	18	17375± 8475 ^{a}	3420± 1525 ^{a}	13955 ± 8826^{a}
Deep soil	9	18072± 7938 ^{a}	2685± 1373 ^{a}	15387 ± 8497^{a}
	N	**PSI (L/kg)**	**Olsen P (mg/kg)**	**pH**
Topsoil	172	169 ± 130 ^{a}	21 ± 16 ^{a}	6.4 ± 0.55 ^{a}
Subsoil	154	189 ± 181 ^{a}	9.4 ± 8.8 ^{b}	6.5 ± 0.50 ^{a}
Deepsoil	76	201 ± 218 ^{a}	5.0 ± 3.8 ^{c}	6.5 ± 0.49 ^{a}
	N	**Clay %**	**Silt %**	**C% (g/g)**
Topsoil	172	20 ± 5^{a}	41 ± 11 ^{a}	2.3 ± 1.0 ^{a}
Subsoil	154	21 ± 7 ^{ab}	39 ± 12 ^{ab}	1.1 ± 0.48 ^{b}
Deepsoil	76	22 ± 7^{b}	36 ± 13 ^{b}	0.66 ± 0.30 ^{c}
	N	**Ca (mg/kg)**		
Topsoil	50	2375± 996 ^{a}		
Subsoil	50	2345 ± 1172 ^{a}		
Deepsoil	25	2596 ± 1253 ^{a}		
	N	***L***	***a***	***b***
Topsoil	117	50 ± 4.3 ^{a}	1.6 ± 0.53 ^{a}	8.2 ± 2.4 ^{a}
Subsoil	108	50 ± 4.3 ^{a}	1.5 ± 0.60 ^{a}	8.3 ± 2.6 ^{a}
Deepsoil	55	51 ± 4.8 ^{a}	1.6 ± 0.67 ^{a}	9.9 ± 3.7 ^{b}
	N	**Redness Index**		
Topsoil	117	1.2 ± 0.71^{a}		
Subsoil	108	1.1 ± 0.68^{a}		
Deepsoil	55	1.0 ± 0.70^{a}		

Different letters indicate significant differences between soil depths sections (Tukey-Kramer HSD pairwise comparisons)

2.4.2 Soil color parameters as proxies for iron oxides

Soil color parameters were associated with various fractions of pedogenic iron (Table 2.2). Fe-ox displayed a significant negative correlation with (*b)* in subsoil (r=-0.59) and deep soil (r=-0.88). Correlation coefficients between (*b*) and Fe-ox increased with soil depth (Table 2.1). A significant correlation was found between lightness *(L)* and Fe-cd. This correlation was positive in topsoil (r=0.70) and negative in subsoil (r=-0.64). A similar trend was observed for crystalline Fe, which was positively correlated with *(L)* in topsoil (r=0.58) and negatively correlated with *(L)* in subsoil (r=-0.71). Soil redness *(a)* was significantly correlated with crystalline iron (r=0.70) in subsoil. Similarly, the redness index was positively correlated with crystalline iron. In summary, the three different measures of extractable iron were significantly correlated with at least one of the soil color parameters used herein.

Table 2.2. Spearman correlation coefficients between soil color parameters and Fe oxides

Color parameter	**Crystalline Fe**	**Fe-ox**	**Fe-cd**
Topsoil (0-10 cm)			
L	0.58*	0.15	0.70*
a	0.49	0.03	0.32
b	0.52	-0.10	0.36
Redness Index	-0.01	-0.06	-0.18
Subsoil (10-50 cm)			
L	-0.71*	-0.08	-0.64*
a	0.70*	-0.36	0.45
b	0.21	-0.59*	0.05
Redness Index	0.74*	-0.01	0.52
Deepsoil (50-100 cm)			
L	-0.37	-0.54	-0.54
a	0.48	-0.20	0.54
b	-0.03	-0.88*	-0.08
Redness Index	0.60	0.08	0.77

* Significant at an alpha level = 0.05

2.4.3 Prediction of PSI

A stepwise linear regression analysis was conducted using standard soil characterization measurements including soil color parameters (*L*, *a*, *b* and *redness index*) as mineralogical proxies. Variables that are not significant in explaining the variability in PSI (P-value > 0.05) were excluded by iterations. Hence, the variables that didn't contribute significantly to improving the regression model predictions were exchangeable calcium, silt, *redness index* and pH. Results indicate that the effective predictors of PSI in topsoil and subsoil were Olsen P, carbon content, and soil color parameters (*a*, *b*) (Table 2.3). On the other hand, in deep soil, clay content appears to be an equally important predictor, and replaced Olsen P (Table 2.3). Thus, the main soil properties controlling PSI in deep soil were clay, carbon content, and soil color parameters (*a*, *b*).

Soil organic carbon and soil redness (*a*) were the major predictors of PSI across the three-soil depths (Table 2.3). A one unit increase of soil organic carbon content led to an associated increase in PSI by 40 L/kg in topsoil, 48 L/kg in subsoil and 47 L/kg in deep soil (Table 2.3). However, a one unit increase in soil redness was shown to be associated with decreases in PSI; 34 L/kg in topsoil, 37 L/kg in subsoil and 43 L/kg in deep soil.

Table 2.3. Parameter estimates of key soil predictors at different soil depths.

	Topsoil		**Subsoil**		**Deep soil**	
Term	**Estimate**	**Prob>|t|**	**Estimate**	**Prob>|t|**	**Estimate**	**Prob>|t|**
Intercept	64	0.0010*	91	<0.0001*	-1.1	0.96
Olsen P	-1.4	<0.0001*	-2.2	<0.0001*	--	--
C %	**40**	<0.0001*	**48**	<0.0001*	**47**	0.0095*
a	**-34**	0.0027*	**-37**	<0.0001*	**-43**	0.0005*
b	7.7	0.0031*	8.3	0.0002*	10.4	<0.0001*
Clay	--	--	--	--	3.8	<0.0001*

The linear regression model fits showed reasonable correlation with PSI across three soil depths, topsoil ($R^2 = 0.46$), subsoil ($R^2 = 0.38$) and deep soil ($R^2 = 0.49$) (Figure 2.1). Multiple linear regression failed to provide accurate estimates of PSI for both Ultisols and Mollisols in topsoil and subsoil, where the predicted PSI values were mostly underestimated. In deep soil, the model fit slightly improved ($R^2 = 0.49$).

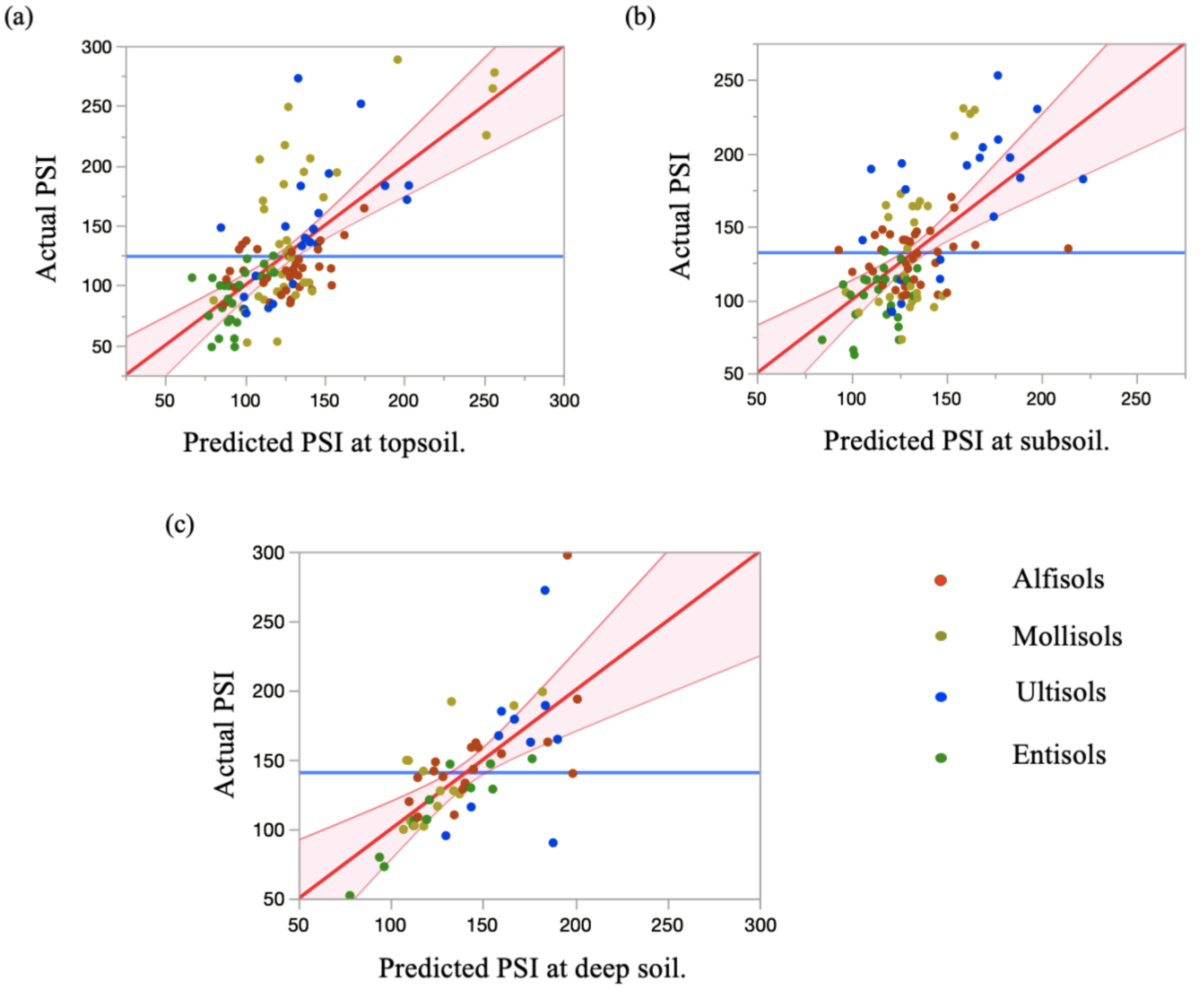

Figure 2.1.Actual versus predicted PSI across different soil depths with a predictive performance of R^2= 0.46 and RMSE= 37 (L/kg) at topsoil (a), R^2= 0.38 and RMSE= 32 (L/kg) at subsoil (b), and R^2= 0.49 and RMSE= 32 (L/kg) at deep soil (c).

Correlation with PSI was strongest when considering the entire soil profile (R^2 of 0.62; Figure 2.2). Soil parameters found to be good predictors of PSI were Olsen P, C% and soil color attributes *(a)* and *(b)* (Table 2.4). The whole soil model was more accurate with an RMSE of 29 (L/kg) **(**Figure 2.2) vs 37 in topsoil and 32 (L/kg) in subsoil and deep soil (Figure 2.1).

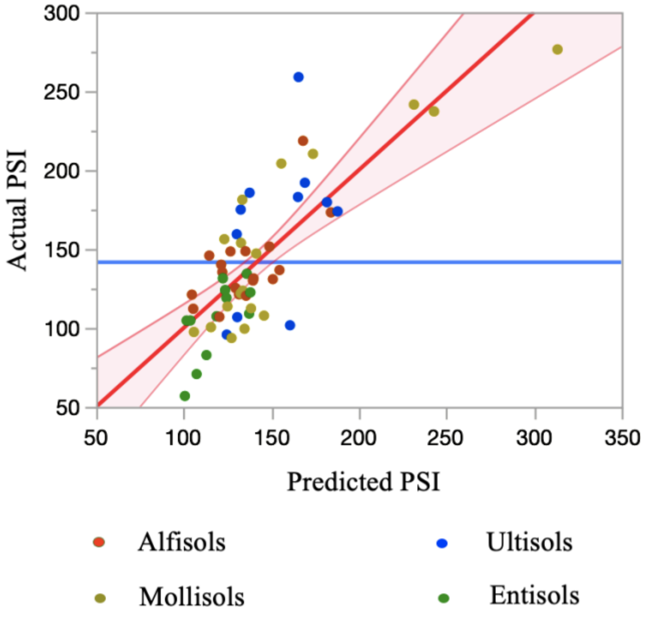

Figure 2.2. Actual versus predicted PSI for whole soil. RMSE= 29 (L/kg), R^2= 0.62

Table 2.4. Parameter estimates of key soil predictors for whole soil depth.

Term	**Estimate**	**Prob>|t|**
Intercept	83	<0.0001*
Olsen P	-2.9	0.0003*
C %	**60**	<0.0001*
a	**-35**	0.004*
b	8.4	0.0007*

Prediction of PSI for the whole soil showed varying degrees of correlation when considering soil orders separately (**Error! Reference source not found.**). The model fit was best for Mollisols (R^2= 0.75). Model fits for Entisols and Alfisols were moderate. However, the model fit was poor for Ultisols (R^2=0.21).

Table 2.5. Multiple linear regression analyses for different soil taxa.

Soil type	Prediction equation	Statistics
Alfisols	$\text{Predicted PSI} = 83 - 2.9 * \text{Olsen P} + 60 * \text{C\%} - 35 * a + 8.44 * b$	R^2 = 0.45; RMSE = 20 (L/kg); Pvalue= 0.0024
Mollisols		R^2 = 0.75; RMSE = 29 (L/kg); Pvalue= <0.0001
Entisols		R^2 = 0.50; RMSE = 18 (L/kg); Pvalue= 0.0104
Ultisols		R^2 = 0.21; RMSE = 45 (L/kg); Pvalue= 0.1583

Removing Ultisols from the overall analysis significantly improved the whole soil model. The R^2 increased to R^2=0.72 and the RMSE decreased to 24 (L/kg) (Figure 2.3) compared to the model using all soil taxa (Figure 2.2). These soils (Alfisols, Entisols and Mollisols had similar mean PSI, but Ultisols had much higher mean PSI and greater variability (Figure 2.4).

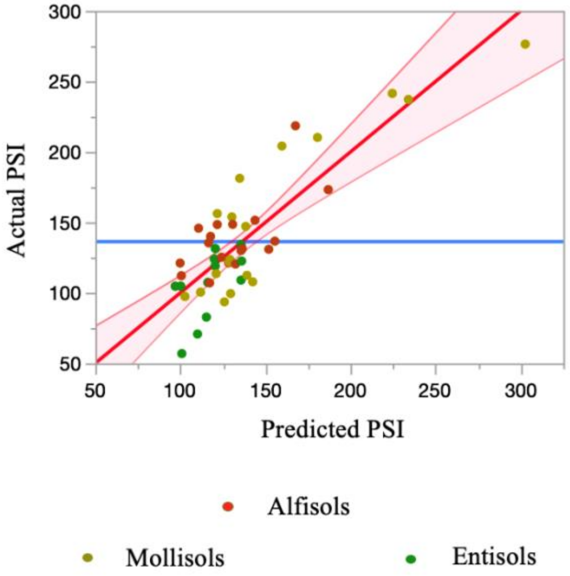

Figure 2.3. Actual versus predicted PSI for entire soil depth and all soil types excluding Ultisols. RMSE= 24 (L/kg); R^2= 0.72.

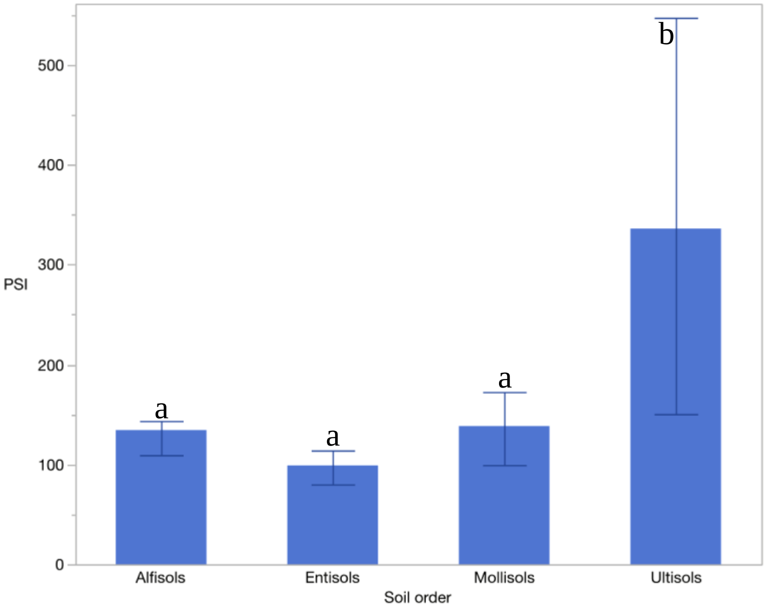

Figure 2.4. PSI (Means ± standard deviations) for the whole soil by soil order.

2.5 Discussion

2.5.1 Standard measurements as proxies for PSI

Significant negative correlation was found between soil yellowness *(b)* and Fe-ox. This result is in accordance with other results of previous research (Kirillova et al., 2015). Soil color parameters (*a*, *b*) significantly influenced the predicted value of PSI, where increasing (*b)* values significantly increased the soils' capacity to fix P. This aligns with similar research suggesting that soil yellowness *(b)* could serve as a proxy for Fe-ox and thus as an affective predictor of P sorption (Scheinost & Schwertmann, 1995). The importance of goethite minerals as key P soprtion sites has been highlighted in several studies, where it was suggested that the affinity of goethite minerals for P adsorption is greater than that of hematite (Guzman et al., 1994; J. Liu et al., 2021).

In contrast to our expectations, increasing soil redness (*a*) led to a decrease in the predicted value of PSI (Table 2.3 and 2.4). This could occur when iron oxide mineral surfaces are coated with soil organic carbon compounds. In fact, when soil organic carbon functional groups (carboxyl, phenols) become sorbed on soil minerals (e.g., goethite), the negative charge on mineral surfaces can increase, and thus, lead to electrostatic repulsion of phosphate (Antelo et al., 2007; Schwertmann et al., 1986). Moreover, soil organic carbon can mask soil redness (Vodyanitskii & Kirillova, 2016) by forming films on iron oxide minerals (Vodyanitskii & Savichev, 2017).

2.5.2 Clay, Olsen P and PSI

P availability is largely related to sorption-desorption processes, which are affected by several soil properties, including soil mineralogy (Fink et al., 2016b). P sorption occurs primarily on Fe/Al oxides (Bortoluzzi et al., 2015; Bromfield, 1964; Freese et al., 1992), yet the role of phyllosilicate clays in P sorption has been broadly neglected (Cui & Weng, 2013; Hinsinger, 2001; Weng et al., 2011, 2012). Our results showed that clay played an important role in predicting PSI, where increasing clay content increased the predicted maximum P adsorption capacity (Table 2.3). This is in agreement with other studies that identified clay minerals as potential sites of P sorption, and highlighted that clay minerals can fix P to the same extent as Fe/Al oxides or even higher (Gérard, 2016; Xiong et al., 2022). Clay played a more prominent role in controlling PSI in deep soil (50-100 cm) (Table 2.3) relative to other depths, where a one unit increase in clay content led to a 3.8 L/kg increase in PSI. This is possibly due to the significantly higher clay content at this soil depth (Table 2.1). Several previous pedotransfer functions identified clay among the most important predictors of P sorption capacity, where increasing clay content is often linked with an increase in P sorption capacity (Dunne et al., 2021; Scheinost & Schwertmann, 1995). In addition to clay content, clay mineralogy has been reported to be critical for P retention (Renneson et al., 2015; Uygur, 2009; Y. t. Wang et al., 2015). A comparative study of P sorption capacity between different clay minerals showed that kaolinite (1:1 clay mineral) and illite (2:1 clay mineral) had differing P sorption capacities. The percentage of P sorbed was estimated at 44% for kaolinite and 52% for illite (Xiong et al., 2022).

In contrast to deep soil, one of the main soil properties that influenced PSI in topsoil and subsoil was available P (Olsen P). For example, a one unit increase in Olsen P resulted in a 1.4 L/kg decrease in PSI in topsoil and 2.2 L/kg decrease in subsoil (Table 2.3). This was expected as near surface horizons are mainly influenced by fertilization. Indeed, studies have shown that long-term fertilization is expected to decrease P sorption capacity (Bhattacharyya et al., 2015; Roy et al., 2017), primarily due to the saturation of available P sorption sites (Barrow & Debnath, 2014; Hughes et al., 2000). Several pedotransfer functions that aimed to predict P sorption capacity or other related indices, such as phosphorus saturation have used available P as a predictor (Kedir et al., 2022; Kleinman et al., 1999; Kleinman & Sharpley, 2002)

2.5.3 Soil organic carbon and P adsorption capacity

The role of soil organic carbon in influencing P adsorption is widely reported in the literature (Debicka et al., 2016; Fink et al., 2016a; Hunt et al., 2007; Kang et al., 2009; Ohno & Crannell, 1996; H. Zhang et al., 2005). Soil organic carbon plays a dual role of either increasing or decreasing P adsorption capacity through different mechanisms, notably (i) the competition between soil organic carbon compounds and phosphate for sorption sites (Ahmed et al., 2019; Y. Liu et al., 2018; Schwertmann et al., 1986; Y. Zhang et al., 2019); (ii) the change of mineral surface charge, leading to an increased repulsion of P anions; (iii) the dissolution of adsorbents, thereby removing P adsorption sites; and, (iv) increase in P sorption sites through formation of cation bridges (Borggaard et al., 2005a; Guppy et al., 2005; Hinsinger, 2001; Hinsinger et al., 2011; Hunt et al., 2007). Our results align with the literature that suggests increasing SOC content significantly increases PSI (Table 2.3). Similar results found a positive relationship between SOC content and the maximum sorption capacity, where increasing SOC can boost soil P sorption capacity (Bera et al., 2006; Debicka et al., 2016; Yang et al., 2019). Addionally, it has been stated that under cultivated soils, P fixation is primarily influenced by soil organic carbon, which could be considered a covariate of different soil management practices (Welikhe et al., 2020).

2.5.4 Comparison with similar studies

P sorption capacity has been evaluated in a variety of soil conditions. Maguire et al., (2001) estimated P sorption capacity of acidic soils in Ireland based on aluminum and iron extracted by oxalate (R^2=0.92). However, this finding is largely a pursuit of mechanisms of sorption since extractable Al and Fe are not properties that are easier or cost effective to measure than PSI. Similarly, a pedotransfer function to estimate P sorption capacity (R^2=0.87) was developed using aluminum and iron extracted by oxalate and citrate dithionite (Borggaard et al., 2004). Using Al and soil organic matter as predictors, Welikhe et al. (2020) elaborated a pedotransfer function to estimate P sorption capacity (R^2=0.60). Compared to these studies, our model, which used commonly measured properties and color as a mineralogical proxy performed well (R^2=0.62-0.72). This outcome suggests that there is a potential benefit for using soil color parameters as proxies for the costly and time-consuming Fe and Al extractions. Thus, they can also be used as effective predictors for P sorption.

The performance of our multiple linear regression model varied across different soil taxa considered in this study. The model fit decreased in the following order: Mollisols (R^2 = 0.75)

<Entisols ($R^2 = 0.50$) < Alfisols ($R^2 = 0.45$) < Ultisols ($R^2 = 0.21$) (Table 2.5). The main difference between Ultisols and all other soil taxa was the significantly higher PSI level in Ultisols (Figure 2.4). When considering all soils except Ultisols, the performance of the regression model increased from R^2=0.62 to R^2= 0.72. This could be related to the complexity of P behavior in various soil types where many soil factors control the extent of P adsorption such as: specific surface area, the concentration and crystallinity of minerals, which in turn are mostly affected by the degree of soil development and nature of parent material (Barrón & Torrent, 1996; Daly et al., 2015; Schaefer et al., 2008; Wilson et al., 2023). Thus, further studies are needed to better understand how soil variability influences PSI, especially in Ultisols.

2.5.5 Implications and future directions

The use of soil color as an indirect attribute of soil mineralogy can be used to improve soil and fertilizer P management (Fink, et al., 2016b). We confirmed the feasibility of using a limited number of easily acquired predictors such as soil color to predict PSI, and to speculate on possible biogeochemical mechanisms. Our work expands upon the idea that soil color can be applied to approaches for precision agriculture (Ibáñez-Asensio et al., 2013). Furthermore, soil color could be considered as a pedoindicator to map for a variety of outcomes including P fertilization guidelines, sorption, and as indicators of risk as sources of P cantamination to water bodies (Baldo et al., 2021).

2.6. Conclusions

This study aimed to predict P sorption index (PSI) using widely available and cost-effective measurements of soil properties across variable soil types. We explored the feasibility of using soil color parameters as proxies of iron oxide content in soils, and as effective predictors to estimate P sorption index (or P sorption capacity). Four routinely measured soil properties, including available P (Olsen P), organic carbon content (C%), redness (a) and yellowness of the soil (b) were selected as potential predictors of PSI . The regression equation showed an overall good performance (R^2= 0.62) when considering all soil types. The model fit increased (R^2= 0.72) when we removed soils (Ultisols) with significantly higher PSI values. According to the results of the regression model, PSI tends to increase with increasing values of soil organic carbon, and soil yellowness, whereas available Olsen P and soil redness were shown to be related to decreased values of PSI. Our findings are particularly relevant to precision agriculture, which demand large sample sizes. In future works, taking into consideration soil management practices and different crop type having different nutrient demand would provide additional insights for understanding PSI variability and improve models predictions.

3.7 References

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Chapter 3 Importance and practicality of soil organic carbon saturation deficit assessment: Case of a chronosequence the viticultural region of Lodi, California.

3.1. Abstract

Storing soil organic carbon (SOC) in recalcitrant or slowly cycling pools, such as the mineral associated soil organic matter fraction (MAOM) could help offset impacts of GHG emissions on climate change. Yet, soils' capacity to store SOC within MAOM does not increase linearly with carbon input. Every soil has a C saturation limit, which varies across different soil types and environmental conditions. Hence the main objectives of this study were to (1) compare the maximum capacity to store SOC as MAOM across a chronosequence of soils having variable degrees of soil development; (2) identify which soils along the chronosequence have the greatest potential to store additional durable C by comparing soil C saturation deficits; and, (3) investigate changes in different SOC fractions (coarse POM_c, fine POM_c, and $MAOM_c$) in response to management practices across the chronosequence. The chronosequence, spanning over 500,000 kyr of soil development, consists of weakly developed soils located on recent alluvial fans (AF), moderately developed soils forming on low terraces (LT), and highly developed soils located on high terraces (HT). The theoretical maximum soil C (C_{max}) that can be stored within the soil fine fraction (< 50 µm) was estimated based on the dominant clay mineralogy in the top 10 cm. Soil C saturation deficit was calculated as the difference between the theoretical C_{max} and current C stored within the fine fraction ($MAOM_c$). Results show C_{max} varied across the different soil types considered in this study, where soils having a high fraction of clay and silt with predominantly 2:1 clay minerals (LT soils) had significantly higher C_{max} (27.40 g/kg) followed by AF soils (22.32 g/kg). Lastly HT soils having a relatively high amount of clay and silt, had lowest C_{max} (17.44 g/kg) due to the mineralogy dominated by 1:1 clays. The current soil C stored within the fine fraction ($MAOM_c$) also varied across soils of the

chronosequence. LT soils had the lowest $MAOM_c$. No difference was observed between HT and AF soils. Similarly, the soil C saturation deficit varied across the chronosequence, where LT soils had the highest soil C saturation deficit. Our results demonstrate that the soils' capacity to stabilize C as $MAOM_c$ can significantly vary depending on soil type and degree of development. Regarding soil management practices, our results showed that changes in SOC within fractions due to compost addition or tillage practices varied depending on soil C saturation deficit. Hence, for soils with low to moderate soil C saturation deficit, changes in soil C were mainly perceived within the $MAOM_c$ fraction (AF) or $MAOM_c$ and coarse POM_c (HT). On the other hand, for soils with high saturation deficit, the main changes were observed within the coarse POM_c fraction. Furthermore, when soils reach the saturation limit, addition of C via soil management practices did not lead to any significant changes within $MAOM_c$. Thus, knowing the soil status vis a vis C saturation level may increase the effectiveness of soil management practices to sequester SOC.

3.2. Introduction

Soil organic matter (SOM) plays a vital role in increasing ecosystem productivity and resiliency of soil, as it improves soil health and helps mitigate the impact of climate change (Georgiou et al., 2022; Hutchinson et al., 2007; Lal, 2004; Lehmann & Kleber, 2015). The importance of SOM has been highlighted and acknowledged in recent policies, such as the healthy soil program and California's climate action plans (CDFA, 2020) and in several of the United Nations Sustainable Development Goals (SDGs), such as SDG #2 (zero hunger), SDG#13 (climate action) (Abrar et al., 2021). Soil contains more organic carbon than the atmosphere and vegetation combined (Fontaine et al., 2007; Jobbágy & Jackson, 2000; Schmidt et al., 2011).

Organic C resides in soil with variable turnover times depending on C fractions (Bernoux et al., 1998). While the labile SOM fraction, also known as the particulate organic matter (POM), has a turnover time of days or months, more stable SOM, or the mineral-associated SOM (MAOM), has much longer turnover times, ranging from years to millennia (Feng et al., 2016; Kögel-Knabner et al., 2008; Trumbore, 2000). Since MAOM represents at least half of the total SOM stock (Cai et al., 2016; Wiesmeier et al., 2014), storing SOC within this more stable SOM fraction is an ideal strategy for agriculture to contribute to California's goals of achieving net zero emissions.

Stabilizing SOC as MAOM$_c$ does not increase linearly with increasing amount of organic C input, but has a saturation limit (Hassink, 1997; Six et al., 2002a; Stewart et al., 2008). When approaching saturation, increasing C inputs lead to a decrease in the rate of SOC accumulation within MAOM$_c$ (Stewart et al., 2007, 2008; West & Six, 2007). Thus, estimating the amount of C that can be stabilized as MAOM$_c$ is crucial to effectively manage soil C sequestration (Di et al., 2017). Yet, most current research projects are still using total organic C as the benchmark for evaluating the effect of soil management practices on soil C sequestration. This might lead to misleading conclusions. A more useful concept, soil C saturation potential, is defined as the difference between the theoretical capacity to stabilize SOC as MAOM$_c$ within the fine fraction and the current SOC content stored within that same fraction (Di et al., 2017). This concept can help identify soils with large C storage potential (Feng et al., 2014) and strategically target them to enhance SOC sequestration across various soil types and management systems.

Management practices such as tillage system, compost addition, plant residue management, and crop rotation can be performed to enhance soil C stabilization. Several experiments investigating the influence of soil management practices on soil organic carbon changes have been performed (Lu et al., 2009; Yu et al., 2012). However, little attention has been directed toward exploring changes within different SOC fractions in soils with varying degrees of soil C saturation deficit. Previous studies of soil C sequestration have revealed high spatial variability in SOC stocks, with some soils having high soil C sequestration potential, while others having net soil C losses (Devine et al., 2022). In fact, SOC preservation is conditioned by the balance between stabilization and destabilization mechanisms. The direction of these processes is affected by the soil's capacity to stabilize additional carbon input, where soils with large SOC saturation potential (large saturation deficit) will potentially favor SOC stabilization mechanisms in contrast to C-saturated soils, where destabilization would be more prominent. Knowledge of the spatial distribution of soil C saturation can lead to focused strategies to target landscapes and specific parts of soil profiles to maintain durable C. Thus, this knowledge would help guide development of better strategies and policies to promote soil C sequestration (Angers et al., 2011).

This research project aims to: (1) compare the maximum capacity to store SOC within the $MAOM_c$ fraction and soil C saturation deficits across a 2-million-year chronosequence that spans a development gradient of weakly developed soils formed in Holocene alluvium to well-developed soils forming since the early Pleistocene; (2) compare soil C saturation deficit across these different soil types to identify soils with large soil C saturation deficit; and, (3) investigate changes in different SOC fractions (coarse POM_c, fine POM_c, and $MAOM_c$) at the different regions of the chronosequence having variable degree of soil C saturation deficit in response to management practices.

3.3. Materials and methods

3.3.1. Description of the study site

Soils were collected from vineyards throughout the Lodi American Viticultural Area (AVA). This region offers diverse soil types developed from erosional and depositional processes associated with large alluvial fans sourced from glaciated terrain over the past 2 million years. Landscapes tend to be younger in the US West, with older and more developed soils to the east. The weakly developed soils form from recent alluvial fans, which are formed mostly from granitic alluvium. Moderately well-developed soils of LT are also derived from granitic alluvium, while soils forming on HT are highly developed, formed from mixed rock sources (Table 3.1). Furthermore, the main difference across soils from these regions is clay mineralogy. The granitic alluvium in AF and LT soils are rich in mica, which weathers to vermiculite (2:1 clays), while HT soils have weathered to kaolinite (1:1 clay) (Minoshima, 2012; O'Geen et al., 2008).

The sampled soils were under different types of tillage practices (i.e., conventional tillage or no- till), and either with or without the addition of compost. Nearly 25% of sampled soils from AF were under no-till management, the rest (75%) were under conventional tillage, and all received compost. Moderately developed LT soils were under two combinations of soil management: conventional tillage with compost addition (60% of the sampled soils) and no-till without compost (40%). Lastly, older HT soils were all tilled, where 33% of the sampled soils received compost and 67% were without compost addition.

Table 3.1. Summarizing table of the main characteristics of the soil regions considered.

Region†	Main Characteristics	Age (years)	Management practices	
			Tillage practice*	Compost
Recent Alluvial fans, coarse-textured, granitic alluvium (AF) (n=24)	- Weakly developed (Haploxerolls & Xerofluvents). - Formed from granitic alluvium. - Coarse-loamy family particle size class. - Superactive cation exchange activity class.	< 80,000	CT No till	Compost added
Low terraces, duripans, granitic alluvium (LT) (n=12)	- Moderately developed soils (Durixeralfs, Haploxeralfs). - Derived from Granitic alluvium. - Fine family particle size class. - Active cation exchange activity class.	130,000 - 330,000	CT No till	Compost No compost
High terraces, mixed alluvium (HT) (n=18)	- Highly developed soils (Durixeralfs and Palexeralfs). - Derived from metasedimentary rocks. - Fine family particle size class. - Semiactive cation exchange activity class.	>600,000	CT	Compost No compost

Content adapted from (O'Geen et al., 2008)

†AF: soils developed on alluvial fans, LT: soils developed on low terraces, HT: soils developed on high terraces.

*CT: Conventional tillage, NT: No till

3.3.2 Soil sampling and physicochemical characterization

Soils were selected based on a stratified random sampling design, with the viticulture regions stratified based on parent material, major soil groups, and terrain (Wilson et al., 2023). Soils were collected from 27 sites in 9 vineyards, with three sites per vineyard throughout the Lodi Winegrape District.

Soil samples were taken from the top 10 cm, between March and June 2011 from three randomly chosen rows in each vineyard. Bulk density of the soil was measured using the core method, and air-dried subsamples were sieved to pass 2 mm sieve to be analyzed for particle size distribution (clay, sand, silt). Soil was fractionated into different sizes coarse POM_c (1000-250 µm), fine POM_c (250-53 µm), and the mineral associated soil organic matter $MAOM_c$ (<53 µm). The procedure of separation was performed using a protocol adapted from (Lee et al., 2009). Total C (TC%) of each fraction and of the whole soil (< 2mm) were determined by elemental combustion (Costech Analytical Technologies, Inc., CA, USA) (Burns et al., 2015, 2016). Mineralogy for clay and silt fractions was determined using X-ray diffraction (XRD). For mineralogical analyses of clay fractions parallel oriented specimens on glass slides were employed. The sample treatments for all studied size fractions included saturation with Mg and K ions followed by treatment of the Mg-saturated sample with glycerol, and by heating K-saturated sample at 550℃ for 2 hours. For X-ray diffraction (XRD) clay samples were mounted on glass slides. XRD analyses were made with a Diano XRD 8000 diffractometer (Diano Corporation, Woburn, MA) employing CuKά radiation fitted with a Ni filter and curved graphite monochromator. Silt fractions were analyzed from powder mounts by XRD.

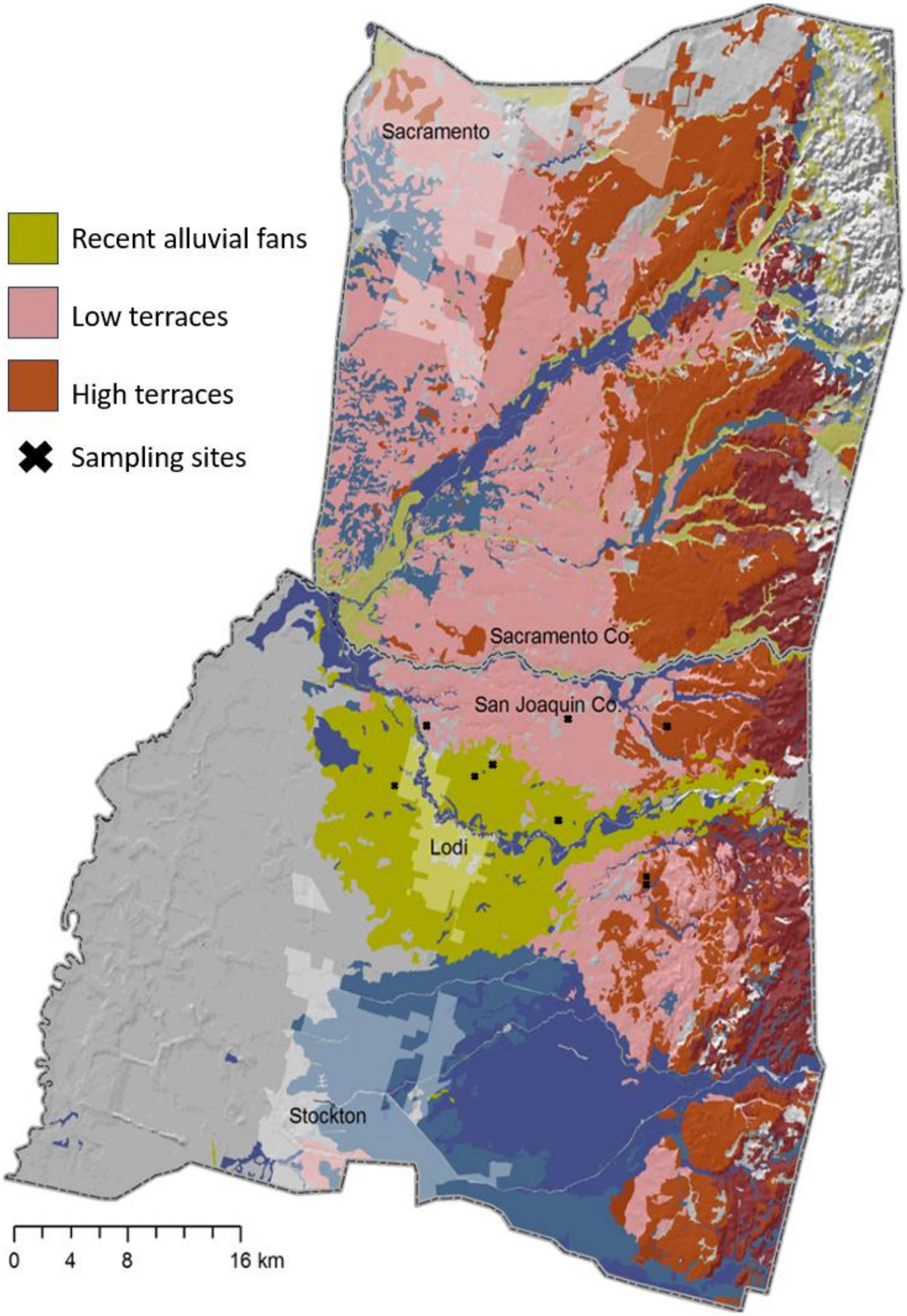

Figure 3.1. Map of soil sampling sites throughout the Lodi American Viticultural Area.

3.3.3 Calculation of soil organic carbon saturation deficit (or saturation potential)

To determine soil C saturation deficit, we first calculated the maximum C (C_{max}) that could be stored within the fine fraction **(**< 53 µm). C_{max} was calculated based on two equations depending on clay mineralogy. C_{max} was calculated using equation 1 for soils dominated by 2:1 mineralogy. C_{max} was calculated using equation 2 for soils dominated by 1:1 mineralogy (Di et al., 2018; Six et al., 2002b).

$$C_{max}\text{ (g/kg)} = 0.21x + 14.76 \text{ for 2:1 clay mineral soils (3), and}$$

$$C_{max}\text{ (g/kg)} = 0.26x + 5.5 \text{ for 1:1 clay mineral soils (4),}$$

where x is the mass proportion (%) of the fine fraction (clay+silt).

The soil C saturation deficit ($SOC_{deficit}$) was computed as the difference between C_{max} and the current SOC stored within the fine fraction (equation 3). The current soil C stored within the fine fraction was measured as the C content within the fine fraction (< 53 µm) ($MAOM_c$).

$$SOC_{deficit}\text{ (g/kg)} = C_{max} - MAOM_c \text{ (5)}$$

The absolute $SOC_{deficit}$ was computed using the following equation:

$$Absolute\ SOC_{deficit}\ (T\ ha^{-1}) = SOC\ deficit\ \left({}^{g}/_{kg}\right) * BD * depth * 0.1 \text{ (6)}$$

where BD is the soil bulk density, 0.1 is a conversion coefficient, and soil depth is 10 cm.

3.3.4 Statistical analysis

To compare soil organic carbon saturation deficit among other key variables (C_{max}, $MAOM_c$, and the fraction of clay and silt) across the soils of the chronosequence, we performed one-way analyses of variances (ANOVA) when variables were normally distributed (C_{max}, $MAOM_c$). For variables that didn't follow a normal distribution (soil C saturation deficit, coarse POM_c, fine POM_c, and the fraction of clay and silt), we used the non-parametric test (Kruskal

Wallis). Significant differences among groups were evaluated using the least significant difference test ($p < 0.05$ level).

Spearman correlation analysis was performed to assess the relationship between absolute soil C saturation deficit and different SOC fractions (i.e., coarse POM_c, fine POM_c, and $MAOM_c$). When variables had a correlation coefficient ($r > 0.50$) and were statistically significant (P-value < 0.05), they were considered to have a strong correlation.

A stepwise linear regression was used to identify the key SOC fractions to be considered as potential predictors of the absolute soil C saturation deficit. The selection criteria were based on variables that were statistically significant (P-value <0.05). All statistical analyses were performed using JMP Pro 16 software.

3.4. Results

3.4.1. Trends in soil physical and mineralogical properties

Physicochemical characteristics and mineralogy varied considerably across the chronosequence. Topsoils from weakly developed AF soils were relatively high in silt (26%) content but low clay (9%). Sand content was the highest among all sites (64%). The mean silt+clay was 36%, which was significantly lower than both LT (60%) and HT soils (46%). In AF soils, the clay fraction consisted mainly of 2:1 minerals (mica), while the silt fraction was mainly mica with trace amounts of kaolinite (Table 3.2). C_{max} (22.32 g/kg) was significantly low compared to LT (27.40 g/kg) but higher than HT (17.44 g/kg). In contrast, TC was the lowest across all sites. $MAOM_c$ was relatively high (17.28 g/kg) similar to HT soils (Table 3.3).

Table 3.2. Particle size distribution and soil mineralogy for topsoil (0-10 cm) within the chronosequence (mean ± standard error).

Soil region	Clay (%)	Silt (%)	Sand (%)	Silt+Clay	Dominant minerals†	
					Clay	Silt
Alluvial fan (AF) (n=24)	9.75 ± 0.58^{a}	26.24 ± 0.73^{a}	64.01 ± 1.14^{a}	0.36 ± 0.01^{a}	M	M, K(tr)
Low terraces (LT) (n=12)	22.67 ± 0.90^{b}	37.54 ± 1.14^{b}	39.79 ± 1.76^{b}	0.60 ± 0.02^{b}	V	M, K (tr)
High terraces (HT) (n=18)	14.15 ± 0.67^{c}	31.77 ± 0.85^{c}	54.08 ± 1.31^{c}	0.46 ± 0.01^{c}	K	M (tr), K (tr)

†M= mica, V= vermiculite, K= kaolinite, tr =trace
Different letters indicate significant differences between regions (Tukey-Kramer HSD pairwise comparisons) at the $p < 0.05$ level

Soils from the moderately developed LT soils had the highest silt (37%) and clay (26%) content, and the lowest sand content compared to AF and HT. Mean silt+clay was 60%, which was the highest among all sites. Clay mineralogy was dominated by 2:1 minerals (vermiculite) (Table 3.2).

Highly developed HT soils had a relatively high clay content (14%) compared to soils in the AF (9%) but lower than soils in the LT (22%). Clay mineralogy was dominated by 1:1 minerals (kaolinite), and the silt fraction had traces of mica and kaolinite. Mean silt+clay was 46%, which was higher than AF (36%), but lower than LT (60%) (Table 3.2).

Table 3.3. Variation of SOC fractions, C_{max} and soil C saturation deficit (g/kg) for topsoil (0-10 cm) within the chronosoquence (mean ± standard error).

Soil region	C_{max} (g/kg)	$MAOM_{c}$(g/kg)	TC (g/kg)	Soil C saturation deficit (g/kg)
Alluvial fan (AF) (n=24)	22.32 ± 0.27^{a}	17.28 ± 0.58^{a}	9.58 ± 0.60^{a}	5.03 ± 0.78^{a}
Low terraces (LT) (n=12)	27.40 ± 0.41^{b}	13.55 ± 0.90^{b}	16.78 ± 0.93^{b}	13.76 ± 1.22^{b}
High terraces (HT) (n=18)	17.44 ± 0.31^{c}	16.63 ± 0.67^{a}	12.30 ± 0.70^{c}	0.81 ± 0.91^{c}

Different letters indicate significant differences between regions (Tukey-Kramer HSD pairwise comparisons) at the $p < 0.05$ level.

3.4.2. Trends in $MAOM_{c}$, C_{max} and soil C saturation deficit across the chronosequence.

Plotting $MAOM_{c}$ relative to C_{max} shows the proximity of the sampled soils to saturation. Approximately half of HT soils exceeded the saturation limit. The other half of samples were 5 to 10 g/kg below saturation. Most AF soils were within 5 g/kg below the saturation limit. However, LT soils were far below the saturation limit (>10 g/kg below saturation) (Figure 3.2). Furthermore, topsoil of this region had the highest capacity to stabilize soil C within the fine fraction (C_{max} = 27.40 g/kg), but significantly lower $MAOM_c$ compared to soils in AF and HT (Table 3.3). Younger soils of the chronosequence (AF) had an intermediate soil C saturation deficit (5.03 g/kg). Soil C saturation deficit increased to 13.76 g/kg in the intermediately aged soils (LT). At the oldest sites (HT), soil C saturation deficit decreased to 0.81 g/kg (Table 3.3). Despite having a relatively high silt+clay content (Table 3.2), the older soils HT had the lowest C_{max} (17.44 g/kg) among all sites, due to the dominance of 1:1 clay mineralogy (Table 3.3).

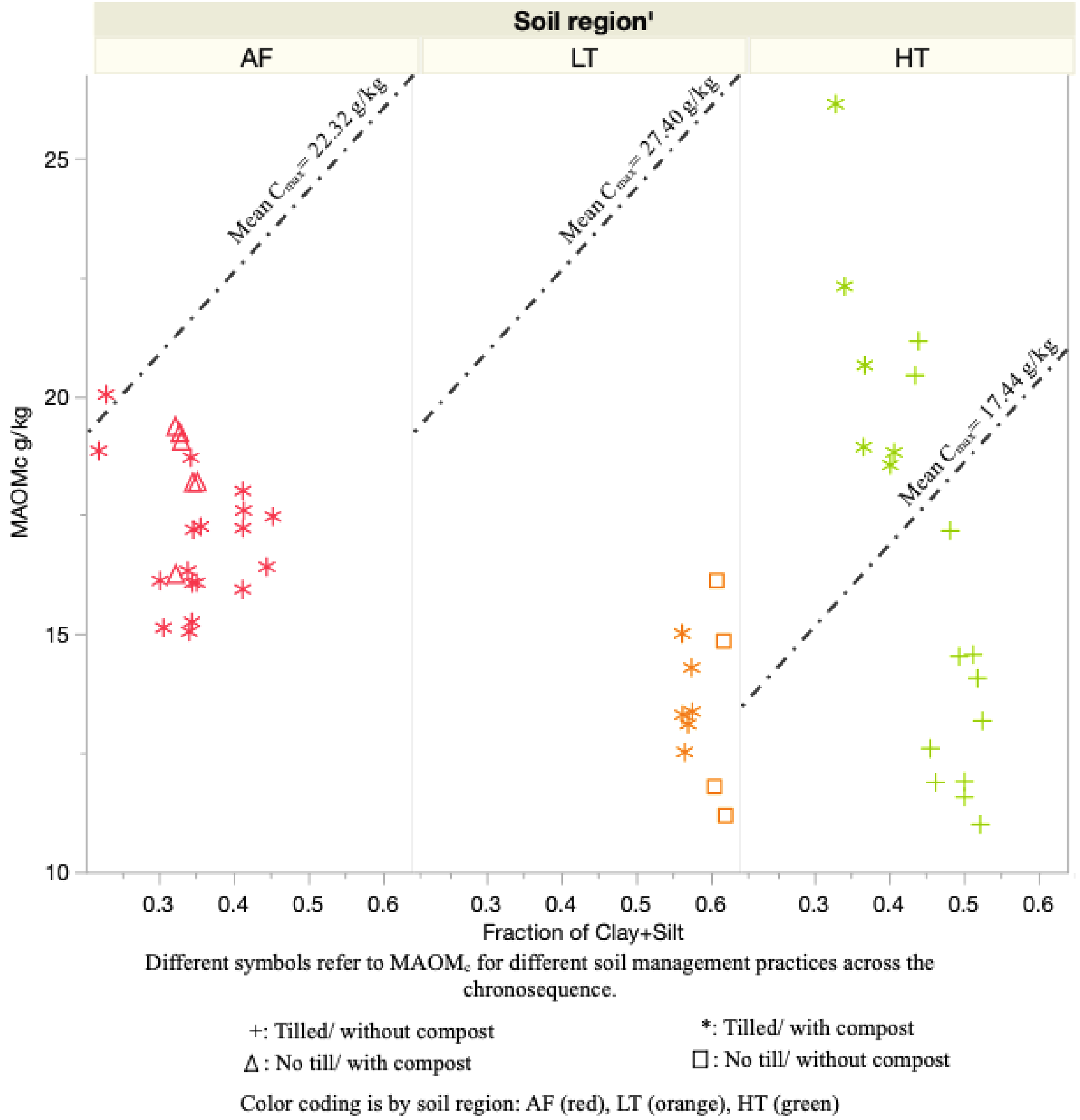

Figure 3.2. Maximum and current soil C ($MAOM_c$) of fine soil particles in soils dominated by 2:1 clay minerals (AF, LT) and 1:1 clay minerals (HT) and under different management practices.

Total carbon (TC) of the younger soils AF didn’t significantly change between till and no-till management. Yet, $MAOM_c$ was significantly higher under no-till than conventional tillage. The mean $MAOM_c$ of soils under no-till was 18.37 g/kg (Table 3.4). This aligns with the results illustrated in Figure 3.2 showing that data points approaching the saturation limit were under no-till with compost addition.

The moderately developed LT soils under no-till and without compost addition had a significantly higher TC content than soils under till and compost addition. Although TC was significantly different between the two sets of soil management, MAOM$_c$ and the absolute soil C saturation deficit showed no noticeable difference between the two sets of soil management practices (Table 3.4).

There was no significant difference in TC between soils with or without compost addition in the older HT soils. Interestingly, all sampled soils receiving compost were 5 to 10 g/kg above the saturation limit (Figure 3.2). Hence, the soil C saturation deficit for soils with compost was significantly lower (1.30 T/ha) than for soils with no compost addition (5.45 T/ha) (Table 3.4).

Table 3.4. Variation of TC, MAOM$_c$, and absolute soil C saturation deficit by soil region and main management practices (mean ± standard error).

Soil region	Management practices		TC (g/kg)	MAOM$_c$ (g/kg)	Absolute soil C saturation deficit (T/ha)
	Tillage practice†	Compost			
Alluvial fan (AF)	CT	Compost	9.52 ± 0.84^{a}	16.93± 0.32^{a}	3.42 ±0.29^{a}
	NT		9.79 ± 0.84^{a}	18.37 ± 0.54^{b}	2.66 ±0.51^{a}
Low terraces (LT)	CT	Compost	13.84 ± 1.11^{a}	13.60 ± 0.66^{a}	7.19 ± 0.61^{a}
	NT	No compost	20.19 ± 1.36^{b}	13.49 ±0.81^{a}	8.74 ±0.74^{a}
High terraces (HT)	CT	Compost	14.04 ±1.23^{a}	20.89 ± 1.33^{a}	1.30 ± 0.84^{a}
		No compost	11.44 ± 0.87^{a}	14.50 ± 0.94^{b}	5.45 ± 0.60^{b}

Different letters indicate significant differences between soil management practices within the same soil region (Tukey-Kramer HSD pairwise comparisons) at the $p < 0.05$ level.

† CT: Conventional tillage; NT: No till

3.4.3. Trends in different SOC fractions for soils across a chronosequence with varying degree of soil C saturation deficit.

A variable trend of different soil C fractions was observed across the chronosequence (AF, LT, HT), which have a diverse degree of soil C saturation deficit levels. For the younger AF soils having a moderate soil C saturation deficit (5.03 g/kg), the influence of soil management was mainly within the MAOM$_c$ fraction whereas coarse and fine POM$_c$ showed no significant difference in response to management practice (Table 3.5). MAOM$_c$ was higher under no-till with no compost compared to tilled with compost.

The intermediately aged LT soils had the highest soil C saturation deficit across all sites (13.76 g/kg) (Table 3.3) and the main differences in soil C fractions in response to management were observed in the coarse and fine POM$_c$, while no significant difference was observed in the MAOM$_c$. Substantially higher values of coarse POM$_c$ and fine POM$_c$ were observed under no till treatment compared to conventional till (Table 3.5).

The older HT soils which had the lowest mean soil C saturation deficit (0.81 g/kg) (Table 3.3), showed a different trend. Significant differences were observed in coarse POM$_c$ and MAOM$_c$, whereas no significant difference was observed in fine POM$_c$. Compost addition was associated with a significantly higher MAOM$_c$ content, whereas no compost addition had a significantly higher coarse POM$_c$ (Table 3.5).

Table 3.5. Variation of different SOC fractions across soils with varying degree of soil C saturation deficit and different management practices (mean ± standard error).

	Management practices		Coarse POM$_c$	Fine POM$_c$	MAOM$_c$
Soil region	Tillage practice†	Compost addition	(g/kg)	(g/kg)	(g/kg)
Alluvial fan (AF)	CT	Compost	3.17 ± 0.24^a	3.69 ± 0.22^a	16.93± 0.32^a
	NT		3.37 ± 0.41^a	3.77 ± 0.38^a	18.37 ± 0.54^b
Low terraces (LT)	CT	Compost	19.05 ± 4.16^a	7.35 ±1.42^a	13.60 ± 0.66^a
	NT	No compost	44.55 ± 5.10^b	18.34 ±1.73^b	13.49 ±0.81^a
High terraces (HT)	CT	Compost	4.38 ± 0.51^a	10.17 ±1.20^a	20.89 ± 1.33^a
		No compost	6.71 ± 0.36^b	9.92 ±0.85^a	14.50 ± 0.94^b

Different letters indicate significant differences between soil management practices within the same region (Tukey-Kramer HSD pairwise comparisons) at the $p < 0.05$ level.
† CT: Conventional tillage; NT: No till

Considering the same soil management type (conventional tillage with compost addition), the different SOC fractions (i.e., coarse POM$_c$, fine POM$_c$, and MAOM$_c$) varied considerably among soil regions of the chronosequence (Figure 3.3). The coarse POM$_c$ fraction was significantly higher in soils with high soil C saturation deficit LT (19.05 g/kg), whereas for soils with low saturation deficit (AF and HT), the content of coarse POM$_c$ was lowest and didn’t significantly differ between AF (3.17 g/kg) and HT (4.38 g/kg) (Table 3.5). MAOM$_c$ was highest in older HT soils (20.89 g/kg). MAOM$_c$ decreased with increasing soil C saturation deficit (AF>LT). On the other hand, fine POM$_c$ was significantly higher in soils with low soil C saturation deficit HT (10.17 g/kg), followed by LT soils with a high soil C saturation deficit (7.35 g/kg) and lastly AF soils with an intermediate level of soil C saturation deficit (3.69 g/kg) (Table 3.5). It seems that there is a variable trend in SOC partitioning into different fractions, suggesting a preferential soil C stabilization that depends on the level of soil C saturation; where soils with the highest soil C saturation deficit LT have the highest content of coarse POM$_c$, while soils with the lowest soil C saturation deficit HT have the highest content in MAOM$_c$.

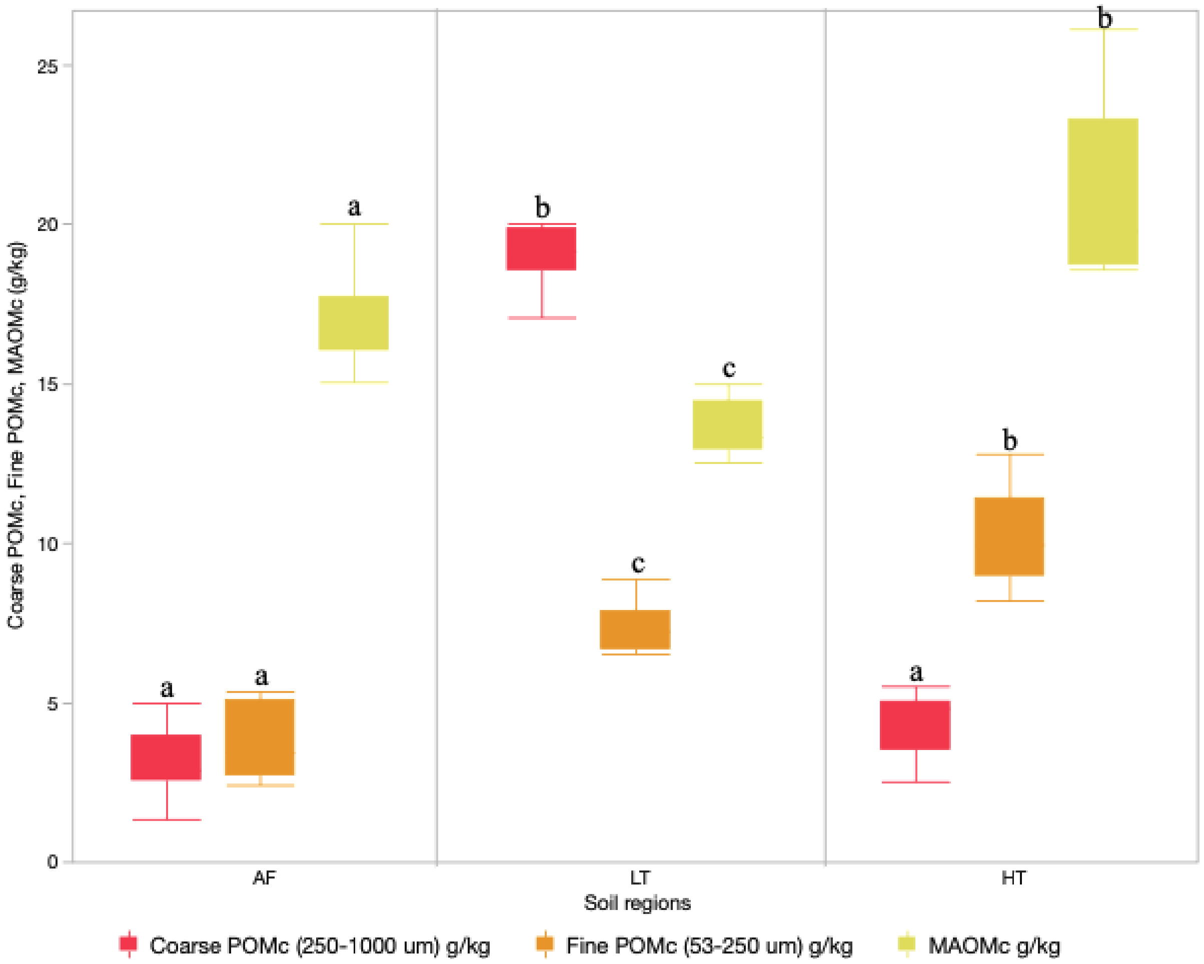

Figure 3.3. Variation of different SOC fractions across different regions of the chronosequence and conventional tillage with compost addition.
Different letters indicate significant differences of SOC fractions across regions of the chronosequence (Tukey-Kramer HSD pairwise comparisons) at P-value < 0.05.

The absolute soil C saturation deficit was not only related to the C content in $MAOM_c$ (r= -0.85; *p* <0.001) but also significantly correlated with the coarse POM_c fraction (r= 0.66; *p* <0.01) (Figure 3.4). Additionally, there was a strong correlation between the different SOC fractions, where the fine POM_c and coarse POM_c were positively correlated (r= 0.81; *p* <0.001). $MAOM_c$ and coarse POM_c were negatively correlated (r= -0.50; *p* <0.001) (Figure 3.4).

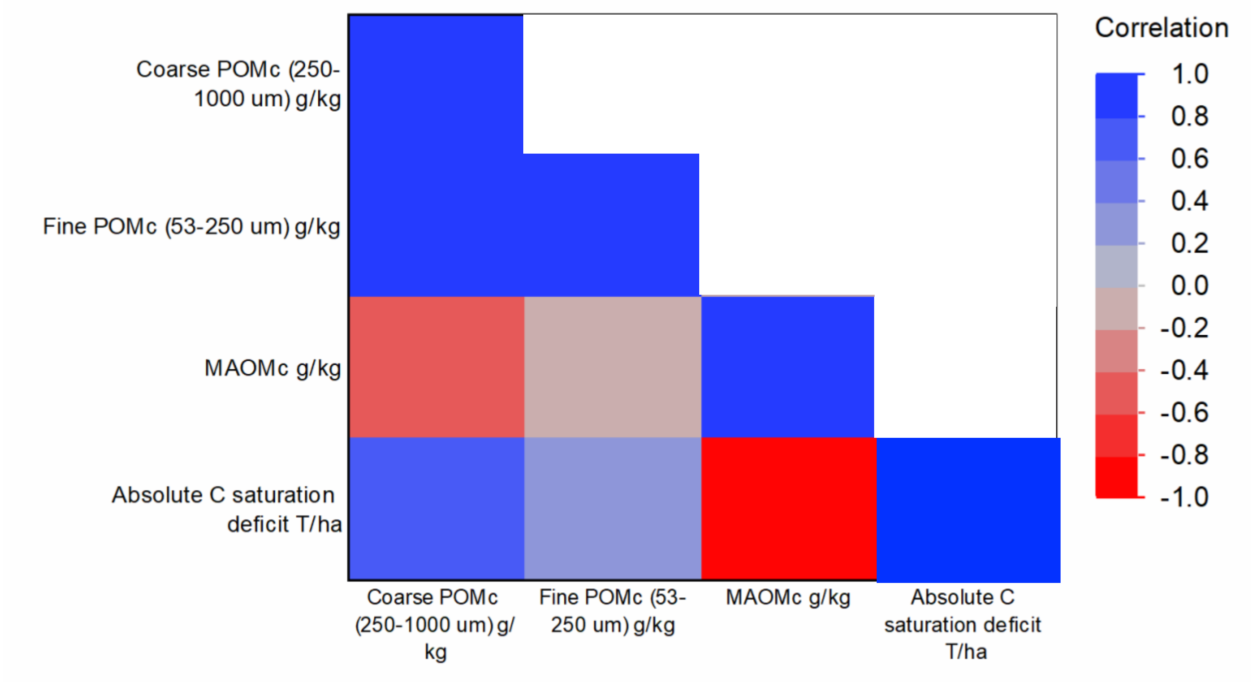

Figure 3.4. Spearman's correlation matrix of absolute soil C saturation deficit and different SOC fractions; coarse POM_c, fine POM_c, and $MAOM_c$.

The strong correlation between the absolute soil C saturation deficit and both SOC fractions, coarse POM_c and $MAOM_c$, was confirmed by the results of the stepwise regression that selected these two fractions as important predictors of the absolute soil C saturation deficit (Table 3.6). Both fractions explain 80% of the variation in the absolute soil C saturation deficit (Figure 3.5). A one unit increase in the $MAOM_c$ leads to an estimated decrease in the absolute soil C saturation deficit by 0.60 T/ha, and a one unit increase in the coarse fraction led to an increase in the absolute soil C saturation deficit by 0.08 T/ha (Table 3.6).

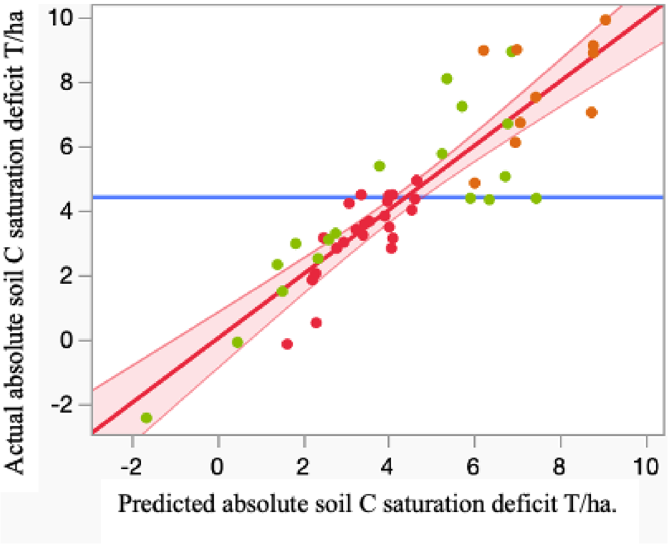

Figure 3.5. Actual versus predicted absolute soil C saturation deficit (T/ha). RMSE= 1.19 (T/ha), R^2= 0.80 Color coding is by soil region: AF (red), LT (orange), HT (green) Blue line refers to the mean of the response variable (absolute soil C saturation deficit T/ha).

Table 3.6. Parameter estimate of the key SOC predictors of the absolute soil C saturation defici*t*.

Term	**Estimate**	**Std Error**	**Prob>|t|**
Intercept	13.29	0.99	<0.0001*
$MAOM_c$ (g/kg)	-0.60	0.06	<0.0001*
Coarse POM_c (g/kg)	0.08	0.01	<0.0001*

3.5. Discussion

3.5.1 Soil mineralogy and its influence on soils capacity to stabilize soil carbon (C_{max})

The soils' maximum capacity to stabilize C within the fine fraction (C_{max}) was mostly influenced by inherent properties. C_{max} differed considerably across all sites of the chronosequence (i.e., AF, LT, HT), where the highest values were noticed in LT (27.40 g/kg) (Table 3.3). This difference was primarily driven by the variation in soil texture and soil mineralogy. This aligns with recent research stating that the amount and type of minerals largely influence C_{max} (Feng et al., 2013; Mikutta et al., 2006; Six et al., 2002b). Similarly, Di et al., (2017) found that soils dominated by 2:1 clay minerals had significantly higher C_{max} than soils dominated by 1:1 clay minerals. Devine et al., (2022) found a significant difference of soil organic matter content in fine-textured soils than coarser-textured regions. Indeed, several studies have indicated that SOC is texture-dependent, particularly the fine fraction (Arrouays et al., 2006; Bosatta & Ågren, 1997; Hassink, 1997). This fraction could be considered as proxy for the mineral surface area available for interactions with SOC (Angers et al., 2011). Thus, the importance of this fraction relies on its role in defining the maximum soil C protective capacity through mineral interactions (Hassink & Whitmore, 1997).

Clay mineralogy influences the specific surface area available for organic carbon sorption (Feng et al., 2013; Kahle et al., 2002; Wiseman & Püttmann, 2005), where soils dominated by clay minerals with high specific surface area (SSA) (e.g., smectite, vermiculite) generally have a high capacity for SOC stabilization within the fine fraction ($MAOM_C$) compared to soils dominated by clay minerals with low SSA (e.g., kaolinite) (Tate & Theng, 1980). In fact, the specific surface area (SSA) of expandible phyllosilicate minerals (2:1 clay minerals) is estimated to reach 800 $m^2\ g^{-1}$ (Carter et al., 1986), whereas the SSA of non-expandible clay minerals (1:1 clay minerals) ranges between 10 and 70 $m^2\ g^{-1}$ (Dixon, 1989). Soil mineralogy is strongly influenced by the degree of soil development, parent material and weathering intensity. Given that time is the magnifier of all soil forming processes, the clay fractions of HT soils were dominated by kaolinite (1:1 clay mineral). Soils from AF and LT are derived mainly from granitic alluvium, dominated by mica that weathers to vermiculite (2:1 clay mineral) in incipient and intermediate stages of soil development (Kittrick, 1973). Our results confirm this close relationship between soil development and soil mineralogy also influences the capacity to stabilize soil C, demonstrating that soils can have systematic capacities to stabilize soil C in CA vineyard systems.

3.5.2 Implications for soil C saturation deficit assessments.

Based on our results, soil C saturation deficit (the soils' capacity to stabilize soil C within the fine fraction) is not the same across different landscapes. This variable pattern of soil C saturation deficit with soil development is mostly influenced by both the soils' inherent properties (i.e., soil texture and soil mineralogy), which dictate the soils' maximum capacity to stabilize soil C (C_{max}) and factors affecting the current soil C stabilized as $MAOM_c$ (i.e., quantity, quality of C input and historical soil management practices). Our results showed that soil C saturation deficit changed considerably across soils with different ages and degree of soil development, where the younger AF soils (weakly developed soils) had a soil C saturation deficit of 5.03 g/kg, the intermediately aged (intermediately developed) LT soils had a soil C saturation deficit of 13.76 g/kg, and the older soils (highly developed) HT soils had the lowest soil C deficit across all sites (0.81 g/kg) (Table 3.3). These differences are largely due soil mineralogical differences, which directly influences soil C saturation deficit. AF and LT were dominated by 2:1 clays, whereas the HT soils were dominated by 1:1 clays. Given that C_{max} changes with soil mineralogy as was discussed in the previous section, soil C saturation deficit also varied following the same trend as C_{max}. In fact, similar findings were found in previous research where soil C saturation deficit in soils dominated by 2:1 clay minerals was significantly higher than soils dominated by 1:1 clay minerals (Di et al., 2017).

Management: Stabilizing soil C as $MAOM_c$ is also influenced by numerous variables including C input, climate, land use and ecosystem management practices, where different land uses and management practices may induce variation in organic C quantity and chemical composition, consequently affecting organo-mineral interactions (Wiesmeier et al., 2014; Yu et al., 2012).

Soil management practices such as tillage system and compost addition could potentially affect the current soil C stabilized as $MAOM_c$.

Our results suggest that the level of soil C saturation deficit could influence the extent of C stabilization as $MAOM_c$. In fact, the younger AF soils had a moderate soil C saturation deficit estimated at 5.03 g/kg, and $MAOM_c$ was significantly higher in soils under no-till compared to tilled soils (Table 3.4). Similarly, older soils HT had the lowest soil C saturation deficit across all sites (0.81 g/kg), $MAOM_c$ was significantly higher under compost addition. On the other hand, the intermediately aged LT soils had the highest soil C saturation deficit across all sites (13.76 g/kg), and $MAOM_c$ did not show any noticeable difference between the two sets of soil management practices (Table 3.4). Similar results were found in recent research indicating that when soils are close to saturation, small C inputs can notably reduce soil C saturation deficit, whereas when soils have a large saturation deficit (i.e., soils far from saturation), small C inputs do not significantly alter soil C saturation deficit (Di et al., 2017). Thus, the effectiveness to stabilize additional durable soil C via compost and no tillage is largely influenced by soil C saturation deficit (Angers et al., 2011; Stewart et al., 2009; White et al., 2014; Di et al., 2017; Georgiou et al., 2022). The choice of soil management practices to optimize soil C sequestration should therefore be place-based. A recent framework developed by Devine et al., (2021) demonstrated its utility to guide regional soil health strategies and expectations (Devine et al., 2022). The study presented herein provides an additional criterion that could be used to group regions depending on their soil C saturation deficit.

3.5.3 Influence of management on soil C partitioning across soil C saturation deficits

Determining the most reactive SOC pools is critical to adjust any management practices in order to optimize soil C stabilization. Our results showed that the most reactive SOC fractions to soil management practices (i.e., conventional till or no till, with or without compost addition) varied depending on soil C saturation deficit. The influence of C addition was mainly observed in the coarse POM_c fraction for LT soils with high soil C saturation deficit, whereas for AF soils with moderate soil C saturation deficit, the main changes were perceived within the $MAOM_c$ fraction (Table 3.5). Finally, for HT soils with low soil C saturation deficit, the main changes were perceived within both coarse POM_c and $MAOM_c$ fractions (Table 3.5). Hence, while the coarse POM_c fraction might be considered as an early indicator of the effect of some soil management practices, $MAOM_c$ can also be an effective indicator especially in soils with low soil C saturation deficit.

Higher POM_c (fine and coarse) content observed under no-till treatment in LT soils with high soil C saturation deficit is in agreement with results of previous studies (Awale et al., 2013; Dou et al., 2008; J. Wang & Sainju, 2014). This was expected as the POM fraction consists mainly of plant residues (Gregorich et al., 2006) and becomes more exposed to microbial decomposition due to the effect of tillage breaking down soil aggregates (Six et al., 2000; Zotarelli et al., 2007).

Furthermore, results showed that when soils are saturated or approaching the saturation limit, which was the case for the younger AF soils and the older HT soils, $MAOM_c$ becomes more sensitive to changes in soil management practices. Unlike the intermediately aged LT soils, the influence of no-till in AF was mainly seen in the $MAOM_c$ fraction, whereas no significant difference was noticed in POM_c (coarse and fine). On the other hand, for the older HT soils, having the lowest soil C saturation deficit across all sites, compost addition mainly influenced the coarse POM_c fractions and the $MAOM_c$ fraction (Table 3.5). Similar results found that one-time compost application led to a significant increase of coarse POM_c and $MAOM_c$ fractions (Atoloye et al., 2022). This could be due to the effect of compost addition on enhancing microbial diversity, which facilitate SOC decomposition and faster enrichment of $MAOM_c$

fraction (Atoloye et al., 2022). When $MAOM_c$ is saturated the accrual C increase is mainly noticed within the POM_c fractions, which is in agreement with other studies pointing out that there is a hierchical soil C saturation depending on SOC fractions, where $MAOM_c$ saturates first (Gulde et al., 2008), and when it saturates, additional carbon inputs accumulate in POM fractions (Cotrufo et al., 2019; Di et al., 2017).

The absolute soil C saturation deficit was found to be strongly correlated with the coarse POM_c fraction and $MAOM_c$, where both fractions explained 80% of the variation of the absolute soil C saturation deficit (Figure 3.5). SOC stabilization processes occur in synergy between the different SOC fractions. For instance, POM plays an important role in soil aggregation, and serves as an energy source for microbial biomass (Gregorich et al., 2006; Six et al., 2000). Furthermore, the microbial by-products produced as a result of SOC decomposition (i.e., necromass) are mainly stabilized through the interaction with soil minerals, forming $MAOM_c$ (Kallenbach et al., 2016; Sokol et al., 2022).

We show that the coupled assessment of soil C saturation deficit and the distribution of different SOC fractions is a key element to consider for a reliable assessment of soil C dynamics and soil C saturation in CA vineyards. Having this knowledge in mind provides additional insights into the extent and efficiency of soil C stabilization and most effective management strategies for C stabilization.

3.5.4. Limitations of the dataset

The empirical results reported herein should be considered in light of limitations. The first limitation is linked to the equation used to estimate the soils maximum capacity to store C within the fine fraction C_{max}. This equation was shown to be less robust, having a low coefficient of determination $R^2= 0.1$ for 2:1 clays and $R^2= 0.4$ for 1:1 clays (Six et al., 2002b). This could lead to an underestimation of C_{max}. Improved equations to estimate C_{max} were developed using the soil fine fraction (<20 um), clay and fine silt (Feng et al., 2013). However, using such robust equations was not possible given that the dataset used for our study lacked data on fine silt. The second limitation concerns the soil sampling depth. Our dataset was constrained to current $MAOM_c$ values for the top 10 cm of soil. Measured values of current MAOMc were needed to estimate soil C saturation deficit, thus deficits were limited to the topsoil (10 cm) where fine silt and clay are relatively low relative to subsoils. For future work, assessing soil C saturation deficit at greater soil depths would provide a more accurate estimate. Lastly, we used estimates of C_{max} that may not be representative of the conditions in California. Estimates of C_{max} may be improved with the use of regression equations from soil data originating from Mediterranean climates and regionally representative soils.

3.6. Conclusion and future perspectives

We show that soil C saturation deficit varies with soil development where soils with varying degree of soil development had a differing capacity to stabilize soil C within the fine fraction. Furthermore, results of this study indicated that when soils are approaching the saturation limit or saturated, small C inputs can lead to significant changes within $MAOM_c$. At saturation limit, the soil C accrual occurs primarily within POM_c fractions. Hence, knowing the status of soil C saturation deficit would be of great importance to better allocate resources and help guide decision makers about the extent of soil C stabilization within different soil landscapes. For instance, when soils are far from the saturation limit, management practices that leads to an increase of $MAOM_c$ accrual would be favored. On the other hand, when soils are saturated or approaching the saturation limit, management practices that would help maintain the level of stabilized soil C would be needed. Additionally, future avenues that could emanate from this research are to assess soil C saturation deficit and the variation of different SOC fractions at deeper soil layer.

3.7. References

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