Summer 2021

Carbon Storage via Mineral Bonding in Subsoils A Review of Soil Processes

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Recommended Citation

Goins, K.(2021). *Carbon Storage via Mineral Bonding in Subsoils A Review of Soil Processes.* (Master's thesis). Retrieved from https://scholarcommons.sc.edu/etd/6472

Carbon Storage via Mineral Bonding in Subsoils
A Review of Soil Processes

by

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Bachelor of Science
University of North Carolina Asheville, 2019

Submitted in Partial Fulfillment of the Requirements

For the Degree of Master of Science in

Geological Sciences

College of Arts and Science

University of South Carolina

2021

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Acknowledgements

Thank you to my committee for your efforts to improve this document.

Thank you to my friends and family for all the support over the course of writing this thesis. Your constant understanding and willingness to listen and keep me working over the last couple years means everything. You all made graduate school a memorable time! Thank you!

Thank you especially to Dr. Lori Ziolkowski, my advisor. I appreciate your guidance, patience, and support that helped me become more self-confident as a scientist. Thank you for being my advisor. I could not have asked for a better one!

Abstract

Soil is an important but often poorly understood portion of the carbon cycle. Soil can store more carbon than twice today's atmosphere, but the factors that control carbon storage are often unclear. Carbon enters the soil through input of organic matter, erosion, and aerosol deposition and is lost mostly via microbial decomposition. Carbon loss in soil is impacted by the chemical composition of organic compounds, environmental factors, and human activities. Furthermore, as climate changes soil, carbon storage may be vulnerable. Although carbon can be stored throughout soil, carbon storage varies with depth. In topsoil, carbon is stored for short periods of time through aggregation of organic compounds with soil minerals, roots, and fungus. Subsoil can store carbon for long periods because of mineral bonding; the process of organic compounds attaching to the surface of minerals and becoming inaccessible to microbes. Organic compounds bind to mineral surfaces in a layered, or zonal, manner based on the polarity and binding strength of the compounds. In addition to the zonal model, mineral bound organic compounds are impacted by mineral structure and cation exchange, which can alter the attachment of organic compounds. The interaction of organic compounds with soil minerals changes with moisture and chemical inputs from plant roots. Recently, the increasing threat of climate change has encouraged attempts to prevent soil carbon loss and increase storage. In order to increase carbon storage and prevent loss, soil mineralogy, soil moisture, and plant roots are important to understand as processes working together to control carbon storage. As such, better systems of soil sampling and routine soil carbon monitoring that take into account soil mineralogy, plant root depth, and soil moisture must be developed to determine how soil carbon loss can be prevented and carbon amounts increased.

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Chapter 1: Introduction

1.1 Carbon cycle and Storage

Soil is a critical component of the carbon cycle and represents the largest portion of terrestrial organic carbon (e.g. Trumbore, 2009). Globally, carbon will move between the atmosphere, ocean, soil, and lithosphere in a process known as the carbon cycle (Figure 1.1). The mechanisms controlling the carbon cycle within soil remain unclear. The main gap in understanding pertains to carbon storage, also known as carbon sequestration when storage occurs for long periods of time. As society looks for solutions for reducing atmospheric carbon dioxide, soil carbon storage is of acute interest because soil can sequester significantly more carbon than humans emit yearly. Soil can store up to 2500 Pg of carbon at the highest estimate, nearly 230 times the 11 Pg of carbon (40 Pg of CO_2) emitted yearly from fossil fuel use by humans (Le Quere et al., 2018). Slowing the flux of carbon between the soil and the atmosphere can reduce carbon loss from the soil and could potentially increase the amount of carbon stored over decade to century timescales.

Although the amount of carbon in soil is less than the ocean or lithosphere (Figure 1.1), soil is important because of the shorter timescales at which carbon is cycled makes soil carbon more likely to be impacted by human activity. For example, soil is thought to have lost up to ~130 Pg of carbon, or 4-5 % of total carbon stored in soil since 1900 (Robertson, 2014; Sanderman et al., 2017). This loss is mainly due to erosion and agricultural tillage (Chappel et al., 2016). As a result of rapid decreases in carbon storage within soil, it has become critical to understand the mechanisms that control soil carbon storage and loss.

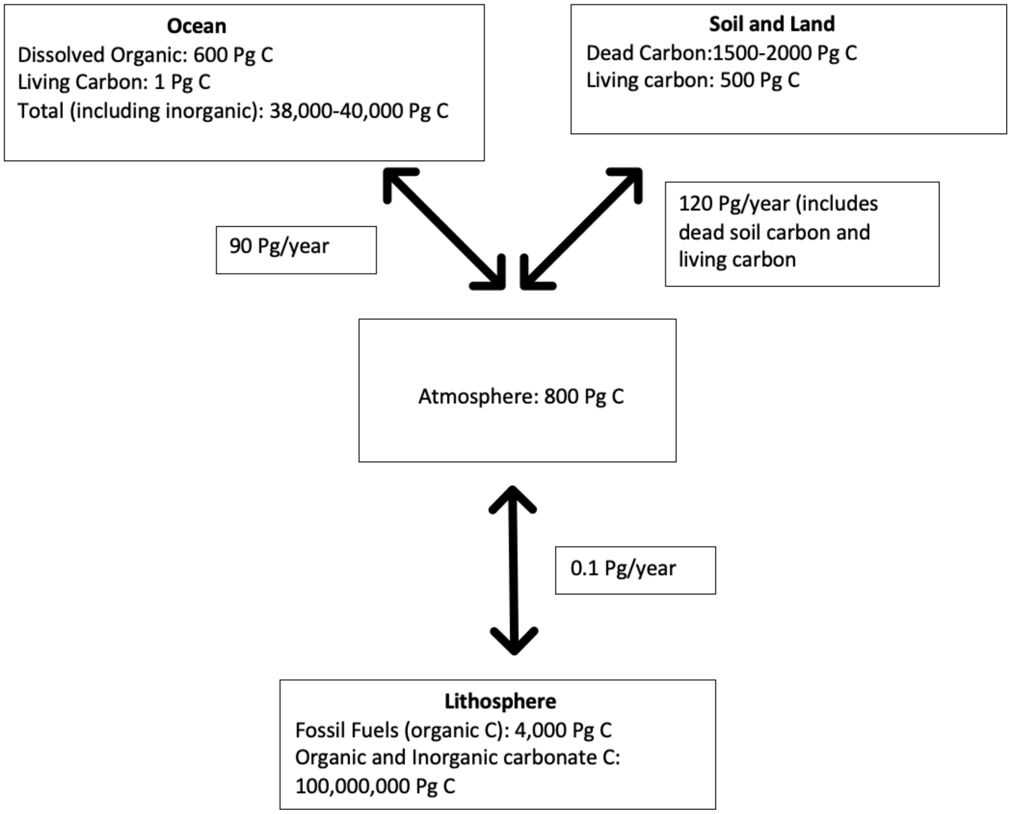

Figure 1.1- Soil carbon cycle with fluxes (arrows) and storage mediums knows as pools. Diagram includes the Pg C of carbon fluxes from the ocean, atmosphere, land, and lithosphere and the amount of carbon stored in each medium (Archer, 2012; Olkers and Cole, 2008; Kansas State University Soil Carbon Center, 2012; and Falkowski et al., 2000).

Carbon storage is the balance between carbon entering (inputs) a medium and carbon loss (Figure 1.2). Most soil carbon enters the soil through root exudates and the decomposition of plant litter, or plant remains that accumulated near the surface of the soil (Leppalammi-Kujansuu et al., 2014).

After death, plants that decompose will release carbon gained from photosynthesis (Lorenz and Lal, 2018). Carbon that is not decomposed by microbes, as well as microbially processed organic matter, can be stored in the soil (Figure 2). Carbon storage occurs when organic matter is stabilized and not rapidly released as CO2. However, stored carbon can be lost over time through erosion, leaching of DOC (organic compounds dissolved in soil water), and microbial respiration, which contributes the largest portion of carbon lost from soil as CO2 (Figure 2) (Trumbore, 2009). Carbon loss primarily occurs in the top 30 cm (Arrouays et al., 2001), due to increased microbial respiration. Carbon storage is more likely occur in soil below 30 cm in depth.

Soil contains a variety of organic compounds that impact how fast carbon is lost from soil. These compounds typically consist of hydrocarbons from plant root exudates, and other compounds produced by microbes during respiration (e.g., Guggenberger et al., 1994; Vives-Pries et al., 2020). Large organic compounds are often broken down by microbes into smaller compounds, which are lost through respiration more quickly than larger compounds. Many organic compounds are also soluble in soil water, known collectively as dissolved organic carbon (Moore and Dalva, 2001; Marschner and Kalbitz, 2003). Compounds broken down by microbes effectively move between different carbon storage pools (e.g. soil to atmosphere) (Figure 1.1), which may lead to increase carbon lost by respiration to the atmosphere or transport of carbon to another parts of the soil. However, the remainder of organic matter will be stored and not immediately released as CO_2 (Condron et al., 2010).

1.2 Research conditions and carbon storage

The magnitude of carbon loss depends on soil conditions, such as mineralogy, that impact microbial decomposition and carbon sequestration. For example, the parent rock of a soil will determine the mineralogy of a soil, soil formation, and speed at which soil is eroded which in turn affect how quickly carbon cycling can occur (Angst et al., 2018). Soil conditions that impact carbon storage also include large scale environmental factors. Environmental factors that impact carbon storage are topography, land use changes (e.g., farm to forest), amount and variety of plant life, temperature, and type of soil, such as sandy or clay soils (Guo and Gifford, 2002; Steinbeiss et al., 2008; Andong et al., 2016). Soil moisture, largely controlled by climate conditions, also impacts carbon storage. Soil carbon storage is a complex process, often requiring many areas of scientific research to understand comprehensively. The soil system is often studied through one aspect of the soil, such as microbial ecology, pedology, chemistry or mineralogy. A narrow scope of research is practical, but may often miss critical balances between varied processes. The lack of communication between sub-disciplines results in gaps in understanding the mechanisms controlling carbon storage. No part of soil carbon storage can be adequately understood through a single lens, especially if soil is to be held up as one potential solution to climate change long term (Hawken, 2017; Wiesmeier et al., 2019). Carbon storage in soil requires a more interdisciplinary approach to research.

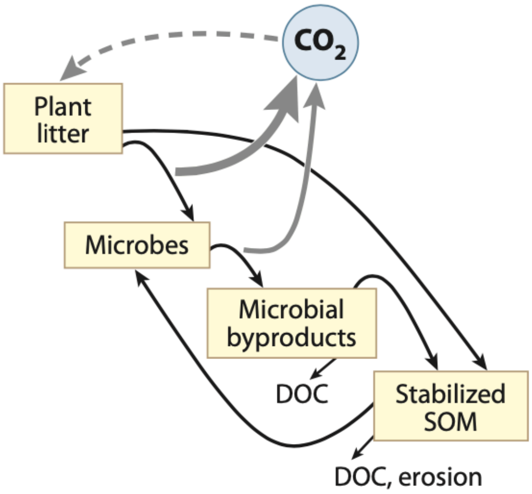

Figure 1.2- The general pattern of carbon loss through microbial decomposition leading to stabilized SOM, or stored carbon (Trumbore, 2009). Carbon storage occurs when stabilized SOM is not rapidly lost from the soil.

The purpose of this paper is to provide a comprehensive look at major components of the soil in terms of chemistry and mineralogy which allow organic matter to remain stabilized in soil. Primarily, the paper will discuss how minerals in the soil are able to retain carbon and the impact of moisture and roots on carbon storage. This will be done by analyzing the role of polarity in how organic matter attaches to mineral surfaces. Additionally, the paper will discuss carbon storage loss through cation exchange and how roots and moisture can increase carbon loss from soil minerals. Finally, the paper will describe how soil carbon can be accounted for and suggest soil attributes that need to be considered to better monitor and potentially reduce soil carbon loss. Ultimately, this paper will view soil carbon storage as a process impacted by geochemical and environmental conditions of the soil.

Chapter 2: Carbon Storage and Soil Stratification

Soil carbon storage is impacted by soil depth. Carbon storage first occurs in surface soils. The majority of carbon storage research is based on data from the top 30 cm of soil because there is more carbon in this layer than deeper soils. However, surface soil is more prone to alterations by human activity (McCarthy, 2005). Surface soil carbon cycling is rapid due to large inputs of easily decomposed organic matter that readily undergoes microbial degradation (Figure 1.2). This rapid cycling creates difficulties in determining precise amounts of carbon stored in surface soil. Deeper soils have a different balance of carbon inputs and losses than topsoil. There is a lower amount of organic carbon in the subsoil, compared to soil above 30 cm (Batjes, 1996; Jobbagy and Jackson, 2000). The magnitude of carbon loss is also much lower than topsoils. As carbon in deeper soil does not cycle as rapidly as surface soil, carbon remains stored for longer periods of time.

In order to understand carbon storage within soil, a system of soil classification must first be established. Soil can be classified in many ways, but for the purposes of this paper, soil will be classified by surface and deep soils. The soil closest to the surface is the topsoil, or soil above 30 cm in depth. Following the topsoil is the subsoil; loosely defined as soil located below 30 cm in depth.

In some instances, subsoil is considered to be soil below 20 cm in depth (Rumpel et al., 2012). The vertical distribution of soil results in different processes between topsoil and subsoil that impacts how carbon is sequestered.

2.1 Carbon Storage in Topsoil

In topsoil, carbon storage occurs primarily through aggregation, a process by which organic compounds are able to avoid microbial respiration by physically attaching to soil particles (Mustafa et al., 2020). Aggregates are a portion of soil that combines minerals, roots, microbial residues, and fungus into a larger structure that creates the main physical conglomeration forming the soil (Six et al., 2004). Initial aggregation occurs between minerals, fungal hyphae, and small remains of plants, forming a microaggregate (Tisdall and Oades, 1982). Over time, increasing amounts of carbon attaches to the microaggregate causing it to increase in size or become a macroaggregate (Tisdall and Oades, 1982).

Carbon estimates in aggregates are complicated by aggregate structural formation. Primarily, the hierarchal formation of aggregates from micro- to macro- does not occur in all soils (Oades and Waters, 1991; Six et al., 2000). Aggregation is also a relatively short term process easily disturbed by physical breakdown from agricultural tillage and soil compaction (Menon et al., 2015), which may reduce the amount of carbon stored in topsoil. However, it is generally unclear how inherent soil properties, such as mineral and carbon content, and age of soil organic carbon affect aggregate formation and associated carbon storage. Estimates of the amount of carbon stored in aggregates is also complicated by the depth at which the aggregates form (Wang et al., 2014).

Most of the soil organic matter is located in topsoil, therefore aggregation is more likely to occur in the top 30 cm. While aggregation is a carbon storage mechanism in topsoil, there is little evidence to suggest that soil aggregates form in the subsoil (Kravchenko et al., 2019). The lack of consistent aggregation formation across soil depths, makes aggregation an unreliable method of carbon sequestration in subsoils.

Current methodology of studying aggregates creates further difficulty in correlating aggregation to carbon storage (Kravchenko et al., 2019). The quantity of carbon within aggregates is based on the size the aggregate is crushed to during lab analyses. Lab methods make it difficult to get accurate estimates of carbon quantities in topsoil, as differing aggregate sizes will result in varying carbon estimates. Furthermore, basic handling of aggregates can result in physical breakdown that can affect carbon estimates. Although accuracy of carbon estimates from aggregation are difficult to assure, globally topsoil is estimated to contain around 200 Pg of carbon (Batjes, 2014), or about one-twelfth of the 2500 Pg total soil carbon estimates.

2.2 Carbon Storage in Subsoil

While topsoil carbon cycling is well understood, carbon found at depth is often not accounted for in carbon storage estimates. This is in part due to poorly defined parameters as to the depth limitations on subsoil. Subsoil carbon estimates are further hampered by the general lack of studies conducted below 1 meter in depth (Rumpel and Kogel-Knabner, 2011; Peixoto et al., 2020). The lack of defined depth parameters for soil carbon estimates creates uncertainties in estimating the total amount of soil carbon present and in understanding carbon loss processes at depth (Trumbore, 2009). Although, carbon loss processes in subsoil are not well researched, there is increased amounts of carbon storage below 30 cm. Subsoil has reduced oxygen and therefore microbial content, which slows carbon decomposition and reduces carbon loss to the atmosphere (Fierier et al., 2003; Rumpel et al., 2012; Yan et al., 2019). Since soil contains organic matter accumulated over time, it takes longer for organic compounds to reach the subsoil than topsoil. Organic compounds that enter the subsoil are often originating from compounds that were not used during microbial respiration in topsoil and make up the compounds in the stabilized portion of organic matter (Figure 2) (Kalbitz and Kaiser, 2008; Kindler et al., 2011; Kaiser and Kalbitz, 2012). Carbon loss due to microbial respiration is therefore reduced in subsoil. Less rapid carbon cycling in subsoil results in increased sequestration of subsoil carbon for longer amounts of time (Harrison et al., 2011).

2.3 Carbon storage and age

Subsoil carbon storage is most easily illustrated by examining the relative age of soil organic matter as a function of depth (Figure 2.1). As exact amounts of subsoil carbon are difficult to estimate; subsoil carbon is studied through proxy factors, such as carbon age. Soil carbon is roughly divided into two broad storage mediums: a fast and slow pool. Pool classification is based on age of carbon and speed of input and loss. The fast pool is measured by the presence of “bomb” carbon, indicating ages of decades (Torn et al., 1997). This

pool has frequent inputs and losses and tends to be closer to the surface with the topsoil containing mostly younger carbon (Figure 2.1) (Shi et al., 2020).
This correlation between radiocarbon content and proportion of new carbon usually occurs regardless of soil type and in most climates (Balesdent et al., 2018). The age of soil carbon usually increases with depth. Deeper soils are depleted in radiocarbon, with little to no bomb carbon, indicating much slower carbon cycling (Shi et al., 2020). Older deeper carbon pools have a mean age upwards of 8000 years (Shi et al., 2020), indicating reduced carbon loss and therefore increased storage.

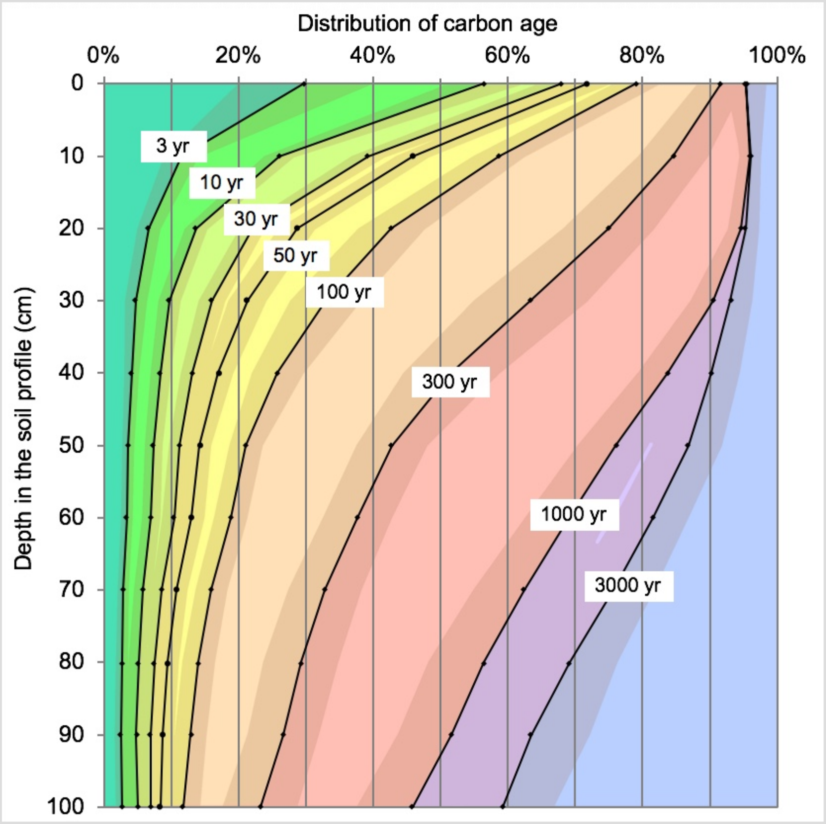

Figure 2.1 – Percent of a soil sample that is new carbon represented by age versus depth. The presence of older carbon indicates that the carbon has undergone less exposure to microbial decomposition and can be used as a proxy for carbon storage. The percentage of older carbon increases with increasing depth, indicating carbon storage is increased (Balesdent et al., 2018).

Chapter 3: Mineral Bonding and Carbon Storage

The role of soil minerals is important to consider when analyzing the processes that impact carbon storage. Soil can maintain carbon through physical processes, such as aggregation, but these stored carbon is often lost from soil quickly due to ease of destruction by physical processes. Soil minerals prevent the loss of carbon by strong chemical attachment of organic matter to a mineral surface, reducing the likelihood of decomposition. Although mineral bonding is the most effective process at maintaining soil carbon, the amount of carbon that is stored on mineral surfaces depends on the chemical composition of the organic matter; cation exchange process that reduce organic matter attachment; and environmental factors, such as soil moisture and roots.

3.1 Mineral Bonding: Definition and Minerals

Subsoil carbon has increased carbon age due to the primary storage mechanism of mineral bonding that reduces carbon loss. Effectively, mineral bonding "freezes" the carbon cycle by limiting the access of microbes to the carbon thereby preventing decomposition. Mineral bonding is a chemical process in which organic compounds attach to certain minerals in the soil (Tisdall and Oades, 1982; Kalbitz et al., 2003; Lutzow et al., 2006; Kleber et al, 2007). Mineral bonding is the main carbon storage mechanism in deep soil (Sollins et al, 2006; Schmidt et al., 2011; Poirier et al., 2020; Solly et al., 2020). The chemical bounding of organic compounds to the surfaces of minerals is known as sorption

(Scheidegger and Sparks, 1996). The likelihood of organic matter bonding to mineral surfaces, depends on the type and structure of the mineral. Sorption primarily occurs on clay minerals (montmorillonite, vermiculite, illite, and chlorite) and metal oxides (hydrous aluminum and iron) (Saidy et al., 2012; Poirier et al., 2020). These minerals are short range order minerals that have an even spacing of iron and aluminum atoms over only a small portion of the mineral structure (Jackson, 1963; Sagger et al., 1994; Kleber et al., 2015). The rest of the structure is amorphous and non-crystalline. The lack of solid crystalline structure throughout the entire mineral surface enables sorption (Sun et al., 2016). An amorphous structure also allows for increased interactions between the factors in the soil environment, such as moisture and roots, and the mineral surface. As a result, large amounts soil organic matter is stored on the surfaces of clay minerals and metal oxides.

The sorption of organic compounds often depends both on the mineral structure and organic matter composition in soil. In a study of temperate conifer forests with similar amounts of annual moisture, similar annual temperature ranges, and in the same climate; mineral content was found to be the defining factor in determining the concentration of CO_2 released from soil (Rasmussen et al., 2008). In this study, organic matter from different pine species was added to soils with varying amounts of short range order minerals. The soil with high concentrations of short range order minerals had less CO_2 emissions (depending on the plant species the carbon input originated) than soil with low short range order mineral content (Rasmussen et al., 2008).

In a separate conducted under similar conditions, soils with higher short range order mineral content, particularly iron oxides, had more than twice the amount of stored carbon as soils with minimal short range order mineral content (Gartzia-Bengoetxea et al., 2020). Due to the decreased loss of carbon from soil with high short range order mineral content, it can be concluded that mineral structure can increase carbon storage by reducing carbon loss from microbial respiration.

3.2 Specific Surface Area and Cation Exchange

Mineral surfaces, plant roots, and moisture interact in a process known as cation exchange capacity (CEC) that determines the impact of soil mineral sorption on carbon storage. Cation exchange is the measure of how many exchangeable cations, such as calcium or potassium, can attach onto a mineral surface or be removed, desorbed, back into the soil (Chapman, 1965; Wan et al., 2020) (Figure 3). Exchangeable cations are cations in solution that are able to substitute for cations on a mineral surface (Sonon et al., 2014). The ability of a cation to attach to a mineral surface is determined by the specific surface area (SSA) of a mineral, or how much space there is for cations and organic matter to bind to a mineral surface. An increased surface area creates an increased amount of space on the mineral surfaces and therefore an increased potential for cation bonding (Macht et al., 2011).

Cation exchange functions as a carbon loss process; controlling both cation and organic matter movement in a soil. Cation exchange is primarily a process for plants to obtain nutrients, in the form of cations, not produced during photosynthesis (Figure 3.1). However, the same process is also a mechanism for altering organic matter sorption onto mineral surfaces (Culman et al., 2019). CEC occurs on clay mineral surfaces and metal oxides with a high specific surface area (Eusterhues et al., 2005). Clay mineral surfaces are negatively charged and can attract positive charged organic compounds (Solly et al., 2020). Cations and organic matter attach to the mineral surface on negative charge sites. As a result of higher specific surface area in clay minerals, there is more space available for organic matter sorption onto the mineral surface. CEC is therefore a proxy for organic matter sorption on soil minerals (Solly et al., 2020). The process of cation exchange on clay mineral and metal oxides moves cations to the roots. The roots then donate hydrogen atoms to fill the charge sites evacuated by the cations (Sonan et al., 2014). This exchange is facilitated by water that moves cations to the mineral surface from the roots and excess cations from roots to clay minerals.

The impact of cation exchange capacity on carbon storage is difficult to determine. This is in part because cation exchange is a reversible reaction process (Chapman,1965). An increased CEC results in increased exchanges of organic matter and compounds from the mineral into the roots. CEC may also decrease the amount of sorption of organic matter on mineral surfaces as a result of this exchange. A decrease in organic compound sorption could result in reduced carbon storage as the organic matter that is not bound to a mineral surface is then subjected to microbial respiration. CEC can have wide ranging impacts on soil carbon storage. Cation exchange is not a process limited to interactions between mineral surface and cations, but instead also encompasses mineral surfaces and plant roots. Furthermore, scientific understanding of CEC in soil is often approached as an ecological problem. There is a limited geochemistry view of organic matter sorption that does not fully explain mineral bonding of organic matter. When CEC is studied from a geochemical standpoint, the roots and moisture in the soil are often not taken into account. CEC is usually understood as a surface interaction affecting where sorption can occur; limiting complete knowledge of mineral bonding as a process impacted by environmental conditions. However, it is necessary to understand both cation exchange and mineral bonding in tandem.

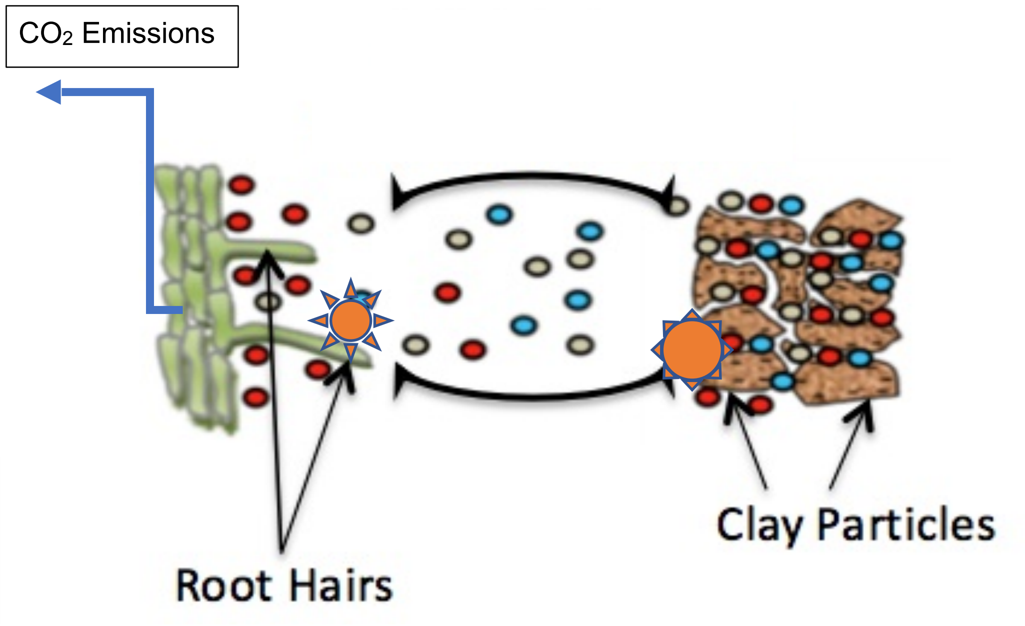

Figure 3.1 - Schematic demonstrating how CEC moves cations (multicolored circles) from mineral surfaces to the roots. Cations move into the roots for use by plants, but organic matter (orange sun shapes) also moves towards the roots. The organic matter is decomposed by microbes and released as CO_2 (Blue arrow). Any extra cations or organic matter is removed from the area around the roots if not being used by the plant. The vehicle for cation and organic matter distribution is moisture (Adapted from Sonon et al., 2014).

3.3 Mineral bonding via the zonal model

In order to understand mineral bonding and cation exchange as related process, it is also important to illustrate how organic matter is bound to mineral surfaces. The zonal model is used to demonstrate how organic matter can layer onto a mineral surface resulting in increased carbon storage depending on type of organic compound. Primarily, the zonal model is used to demonstrate that a layered process of carbon storage is occurring on clay mineral surfaces (Kleber et al., 2007). The compilation of the zonal model marks a paradigm shift in illustrating mineral associated carbon sequestration. Previous models of mineral bonding suggested organic compounds bond to mineral surfaces in single layers that will coat the entire mineral (Mayer, 1994). Monolayer bonding is likely an inaccurate representation of mineral bonding (Kleber et al., 2007). Aluminosilicate clay minerals have been found to have less than 15 percent of total surface covered by organic matter, however organic matter typically accumulated in significantly thicker layers once surface coverage of organic matter was at capacity (Kleber et al., 2007). This gap is explained by vertical stacking of organic compounds into layers onto the mineral surface (Arnarson and Keil, 2001; Kleber et al., 2007), providing evidence for the existence of the zonal model on mineral surfaces. Furthermore, the zonal model can be also used to explain how mineral surfaces with low amounts of sites for organic matter sorption have the same amount of carbon as more clay rich soils (e.g. Araujo et al., 2017).

The zonal model can demonstrate interactions occurring between the surface of minerals and organic compounds. Primarily, organic compounds are bound to the mineral surface through sorption. Carbon storage of organic compounds onto mineral surfaces is also impacted by entropic interactions between organic compounds and polarity (Mitchell et al., 2018). Hydrogen bonding is occurring between compounds closer to the mineral surface, in addition to sorption of organic compounds on the mineral surface (Kleber et al., 2007). Binding is also occurring between organic compounds not directly sorped onto the mineral surface. Binds between organic compounds are maintained when there is high energy required to break the chemical binds between compounds. Polarity primarily influences where organic compounds will attach onto the mineral surface (Chassin,1979; Weber et al., 1983; Kleber et al., 2007). Differing polarities of organic compounds result in mineral bonding occurring in a layered or zonal manner on the mineral surface (Kleber et al., 2007). This can be thought of as the Wershaw bilayer model or a micelle that is made with the organic material from decayed plant proteins, microbial lipids, and other compounds that have both a polar and non-polar end that are on top of a mineral surface (Wershaw, 1986; Kleber, 2007).

The first zone in the model is the contact zone (Figure 3.2). This layer usually contains mostly aromatic compounds and iron oxides along with parts of compounds with both a polar and non-polar end (Kleber et al., 2007). On high charged mineral surfaces, aromatic compounds are in direct contact with the mineral surface. In low charged or no charged mineral surfaces, such as smectites and kaolinites, organic matter will only bond if a protein layer is first added (Kleber et al., 2007). In one study, it was found that the addition of proteins to certain mineral surfaces can increase the sorption of organic acids, such as phenolic acid (Gao et al., 2017, 2018). Organic matter in the contact zone is least likely to undergo desorption and contributes most to carbon storage because organic compounds in the contact zone are held directly to the surface through mineral bonding and can attach to other compounds through hydrogen bonding (Kleber et al., 2007).

The second zone is the hydrophobic zone (Figure 3.2). While this zone and the contact zone both contain non-polar compounds, the hydrophobic zone is distinct as this zone contains mainly hydrocarbons and non-polar compounds with no metal oxides. The hydrophobic zone functions most similar to the Wershaw micelle model (Wershaw,1986). This zone gives further protection to contact zone compounds as a second non-polar layer protected from desorption (Kleber et al., 2007). The hydrophobic zone is highly disordered and compounds are bonded both to the contact zone and polar outer region via entropic interactions (Kleber et al., 2007). Carbon in the hydrophobic zone is also difficult to remove and contributes to carbon storage. Mineral bonding in the hydrophobic zone depends on relatively stabilized conditions within the soil. Any change in the amount of organic matter, pH, or moisture may cause gaps in the layers (Kleber et al., 2007), which will disrupt zonal bonding and expose previously protected layers to potential desorption and carbon loss.

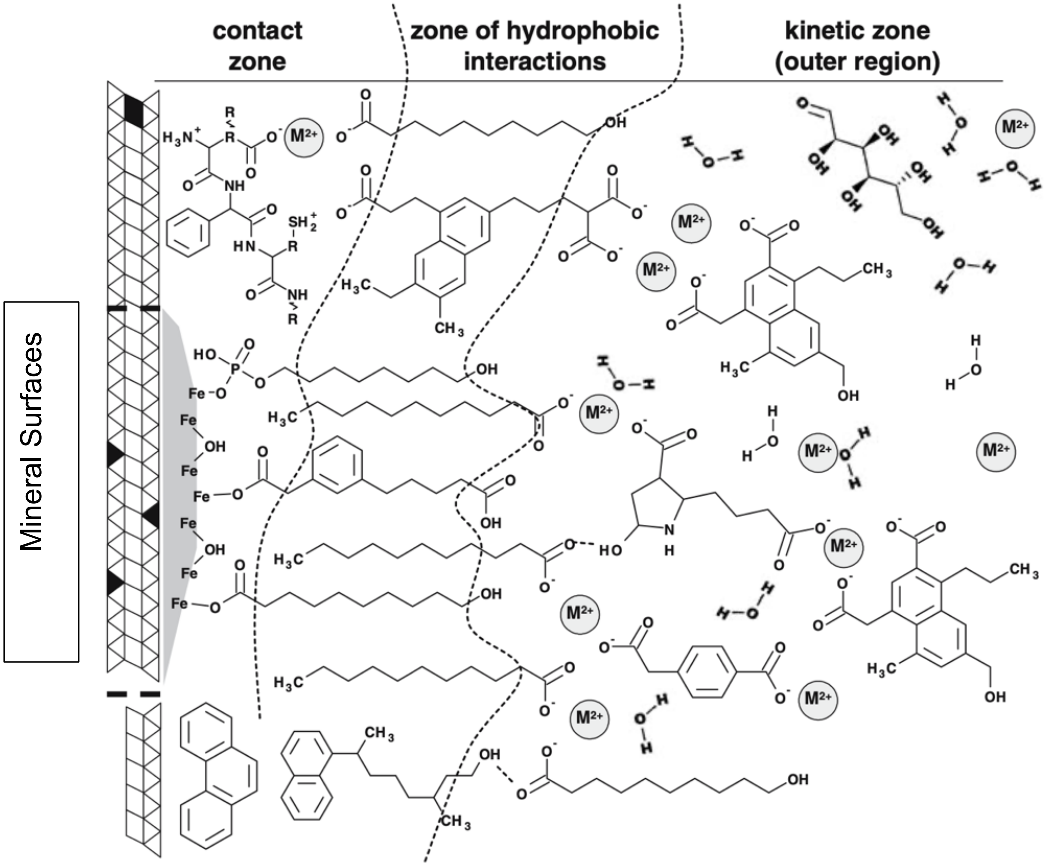

Figure 3.2 – The zonal model with organic compounds grouped by polarity. There a parts of compounds with polar and non-polar ends, as well as aromatics and iron oxides are attached to the mineral surface (left). The hydrophobic zone (center) is a similar composition to the contact zone, but does not contain iron oxides. Polar compounds are in the outer zone (right). The sorption of the compounds onto the mineral surface depends on number and type of charge sites as polarity of the functional group of the compound (Kleber et al., 2007). In a mineral surface that has a low number of charge sites, a protein layer must first be added on top of the mineral surface (shaded center left) for bonding to occur.

The third zone is the polar zone. Polar compounds in the kinetic zone are in a state of constant flux between the soil and the mineral surfaces. Compounds in the kinetic zone are numerous and varied, with a mix of metal cations and many other functional groups (Kleber et al., 2007), including hydrocarbons and a small amount of aromatics (Figure 3.2). These compounds are generally considered amphiphilic, having both a polar and non-polar end (Gao et al., 2019).

Water can also be found within the kinetic zone (Figure 4) as this zone needs moisture to coordinate the flux of compounds undergoing sorption and desorption from the mineral surface and other zonal layers. The kinetic zone is the zonal layer most impacted by increases in carbon and water.

Composition and amount of carbon input determines compound position within the zonal model, the thickness of the zonal layers, and the number of layers that are bound to the mineral surface. Low inputs of specific types of carbon could result in discontinuous mineral bonding of organic matter with not all three layers being present over the entire mineral surface or at any given time (Kleber et al., 2007). However, an increased abundance of organic compounds would increase the thickness of the kinetic zone (Kleber et al., 2007). An increase in carbon in the kinetic zone provides more protection to the non-polar compounds in the hydrophobic and contact zones, and increases the amount of carbon in all three layers as non-polar compounds will migrate closer to the mineral surface (Kleber et al., 2007). However, there are uncertainties within the zonal model. For example, the dividing lines between the layers are not well established and highly disordered with no clear boundary between zones (Possinger et al., 2020). Further, buildup of organic matter may eventually reach a point where mineral surfaces are saturated with carbon and cannot adsorb more organic matter. This could potentially weaken organic mineral bonds in an effect commonly referred to as the carbon saturation threshold (Feng et al., 2014).

3.4 CEC should be studied with the zonal model

Although the zonal model is useful for illustrating how organic matter is stored through entropic interactions and mineral bonding, it is also important to understand that entropic interactions and the zonal model are not the only factors that impact mineral bonding of organic matter. Cation exchange governs the sorption of organic matter onto mineral surfaces (e.g. Kaiser et al., 1997; Gu et al., 1994; Feng et al., 2005), however the impact of CEC on the zonal model is not well understood. This is in part because the role of CEC in mineral bonding is varied and some evidence indicates that CEC may not matter for compounds in hydrophobic and kinetic layers. For example, a study indicated that clay minerals of kaolinite and montmollernite have different SSA and CEC (Mitchell et al., 2018). These minerals are able to sorb differing amounts of organic compounds and would have different amounts of carbon storage. However, as carbon built up on the mineral surface, organic matter attached to the kaolinite and montmorillonite had similar entropic interactions and possibly similar amounts of carbon storage (Mitchell et al., 2018). Effectively, this study demonstrates that as mineral surfaces become more saturated with carbon, entropic interactions between the organic compounds are more likely to bind organic compounds in a zonal formation than sorption of organic compounds onto a mineral surface (Mitchell et al., 2018; Kleber, 2007). The binding of organic compounds will prevent desorption and minimize subsequent carbon loss (Mitchell et al., 2018; Kleber et al., 2007). In this view, there is limited use for CEC as a proxy for carbon storage, as binding is more important for carbon storage than CEC.

However, cation exchange should not be treated as a process only occurring on mineral surfaces. There are a large variety of binding mechanisms between organic compounds (Sanderman et al., 2014) that impact carbon storage within the hydrophobic and kinetic zones. The differing strengths of different types of entropic interactions between organic compounds will result in the zonal layers having different degrees of susceptibility to desorption (Sanderman et al., 2014). As a result, there will be differing degrees of impact of mineral bonding on carbon storage (Sanderman et al., 2014). Cation exchange needs to therefore be considered as impacting carbon storage within the zonal model. For example, the compounds in the contact zone have strong entropic interactions, such as hydrogen bonding, between the organic compounds and mineral surface (Kleber et al., 2007). Carbon in the contact zone would then increase carbon storage (Figure 3.3) as the bonding mechanisms would suggest that compounds in the contact zone are not subjected to CEC and are therefore hard to remove from the mineral surface.In the kinetic zone compounds are indirectly bonded to mineral surfaces from weak entropic bonding forces (Kleber et al., 2007). Weaker entopic interactions in the kinetic zone results in increased potential for desorption (Kleber et al., 2007). The majority of desorption and carbon loss from mineral bonded organic matter may be from organic compounds in the kinetic zone. The process of CEC results in desorption and sorption of organic matter occurring simultaneously within the zonal model (Figure 3.3).

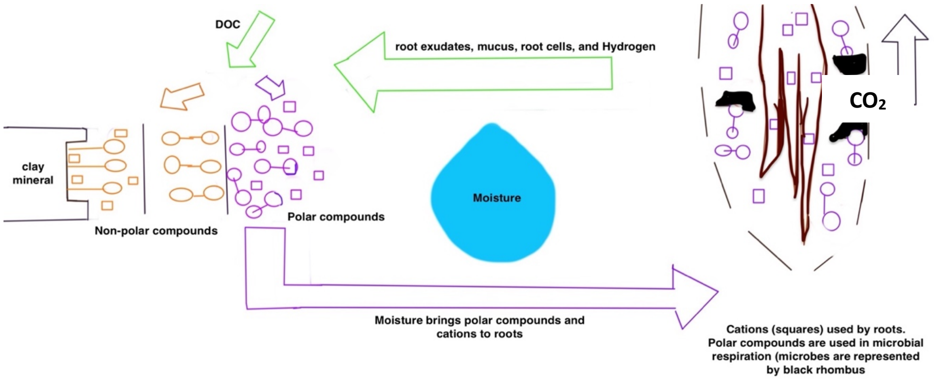

Figure 3.3 – Schematic of zonal bonding interacting with moisture and exhibiting both carbon storage and release for a clay mineral. DOC and root exudates (green arrows) are the primary sources of organic compounds and bind onto the mineral surface based on polarity. While non-polar compounds (orange) are stored via mineral bonding, polar compounds (purple) are able to be decomposed by microbes (black rhombus) as a side effect of CEC near roots (brown shapes). Cations are purple or orange squares. Purple cations are used by roots for nutrient supplementation. Orange cations remain inaccessible to roots and are directly attached to the mineral surface.

3.5 Mineral bonding: methods

In order to understand that the zonal model and cation exchange should be researched in tandem, it is first necessary to understand how mineral bonding is quantified. It is important to note that CEC is quantified separately from mineral bonding, in part because CEC depends on extraneous and changeable soil conditions, such as pH. CEC is usually quantified by ionic strength (e.g. Sumner and Miller, 1996). However, mineral bonding is studied using density fractionation coupled with spectroscopic techniques, such as x-ray (Kreyling et al., 2013; Liu et al., 2013; Poirier et al., 2020). Synchrotron X-ray diffraction (SXRD) is used to determine mineral composition and identify minerals within a soil. Synchrotron X-ray diffraction is the most common form of x-ray used to identify soil minerals, because of the ease at which SXRD can separate parts of the soil complex into distinct wavelengths. SXRD can therefore assist in identifying minerals within a chemically complex soil, where mineral composition is otherwise difficult to separate from other components of the soil (Sharma and Hesterberg, 2020).

SXRD has been used to identify differences in mineral composition in soil impacted by fires. In Australia, this technique assisted in determining the impact of fire on amounts of aluminum and iron in topsoil and subsoil (Yusiharni and Gilkes, 2012). The results of this study indicated that heat causes mineral dissolution and loss of bound carbon from iron and clay minerals as aluminum concentrations were higher in burnt soil in contrast to unburnt soil (Yusiharni and Gilkes, 2012). Unburnt subsoil contained higher amounts of iron as well, indicating carbon would likely be more stabilized on mineral surfaces before a fire than immediately after. Soil type is also important, with most mineral composition changes occurring in soil containing minerals with high specific area (clays) (Yusiharni and Gilkes, 2012). Effectively, SXRD can demonstrate that changing mineral composition will likely impact the amount of carbon stored or lost from a soil. There will likely be an impact on cation exchange and organic matter movement in soil with altered mineral composition; highlighting the need for cation exchange to be explored more in context of mineral bonding and carbon storage.

Density fractionation is another effective method of studying mineral bonding because mineral bonding usually occurs in the densest fractions of the soil (Poirier et al., 2020). In subsoils, sequential density fractionation is used to determine how much organic matter is associated with specific minerals (Poirier et al., 2020). Density fractionation works by dividing samples at all depths into density fractions up to 2.6 g cm^{-3} based on mineral content of bulk soil samples as taken from instruments such as X-Ray spectroscopy (Jones and Singh, 2014). Density fractionation of subsoil has indicated that high density fractions are associated with minerals and likely contain sequestered organic material regardless of topsoil or subsoil (Poirier et al., 2020, Jones and Singh, 2014). Density fractionation also revealed that there was more mineral bonded organic matter in subsoil than top soil. Denser parts of subsoil have higher mineral amounts than topsoil and contained higher carbon concentration than in topsoil (Poirier et al., 2020).

Once the bulk soil has been density fractionated, it is easier to analyze for organic carbon and mineral content. The organic carbon composition is commonly studied using nuclear magnetic resonance (NMR). NMR allows for an assessment of organic compounds within the soil and does not require risking potentially incomplete extraction of organic matter (Kogel-Knabner, 1997). NMR is particularly useful for analysis of soil samples containing smaller size compounds, such as oxalic acid (Preston, 1996), that may be lost in other extraction methods. The mineralogical content of soils can change the effectiveness of using NMR to study the organic carbon composition. Since clay rich soils store larger amounts of carbon, NMR is of most use in clay rich soils (Belesdent and Mariotti, 1996; Christensen, 1996; Kogel-Knabner, 1997). In soil with lower amounts of clay, there is often less carbon stored and NMR becomes difficult to use (Kogel-Knabner, 1997). In order to quantify the how organic carbon may be interacting with minerals, density fractionated soils are often subjected to X-ray photoelectron spectroscopy, which can provide information on the surface composition of the minerals (e.g. Jones and Singh, 2014). NMR and Xray data of the density fractionated soils can be combined to provide insight into the organic matter and mineral composition of soil.

Chapter 4: Moisture

4.1 Compound orientation and polarity

The magnitude of soil carbon loss due to desorption is dependent on environmental factors such as moisture. Water in soil interacts with organic matter in two ways. First, water moves organic matter throughout the soil (e.g. Newcomb et al., 2017). Additionally, organic compounds impacted by zonal model layering on mineral surfaces are usually dissolved in soil water and will often have both polar and non-polar functional groups (Gao et al., 2019). As a result, sorption of organic compounds across a mineral surface varies by the orientation of attached organic compounds facing soil water and will determine if carbon storage can occur (Figure 4.1) (Doerr et al., 2000). For example, organic compounds that are hydrophobic will have a non-polar functional group directed towards water. As non-polar compounds are repelled by water, the mineral surface will become hydrophobic and adsorption of water will become difficult (Mao et al., 2019).

The polarity of a mineral surface is determined by entropic interactions between the dipoles of different organic compounds when reacting to water (Mainwaring et al., 2013), as well as position within the zonal model. The spatial distance of organic compounds from a mineral surface can also impact the polarity of a mineral surface. For example, weaker binds are more common as compounds approach the kinetic zone (Figure 3.2) (Daniel et al., 2019).

Compounds in the kinetic zone are also usually more polar. As a result, compounds in the kinetic zone will be removed into the soil faster than compounds in the inner layers. Desorption of polar compounds, as a result of exposure to moisture, will often leave only non-polar compounds facing the soil water (Gao et al., 2019). This can create mineral surfaces that are non-polar (Gao et al., 2019). As a result of hydrophobicity, compounds on mineral surfaces are resistant to the removal of organic compounds that occurs as a result of cation exchange and moisture exposure. Compounds in the hydrophobic zone with polar ends may then reorientate to have the polar functional end facing the water (Figure 4.1), oscillating the mineral surface between a polar and non-polar mineral surface (Doerr et al., 2000). However, hydrogen bonding and other strong entropic interactions that are occurring between the mineral surface and compounds in the contact or hydrophobic zone (Kleber et al., 2007) would prevent complete desorption of non-polar compounds into the soil. As a result, there would be increased carbon storage on the mineral surface. The full impact of moisture adsorption on soil minerals is ultimately beyond the scope of this paper, but a basic overview of soil moisture is required to understand a critical environmental condition, water repellency, that can impact soil carbon storage.

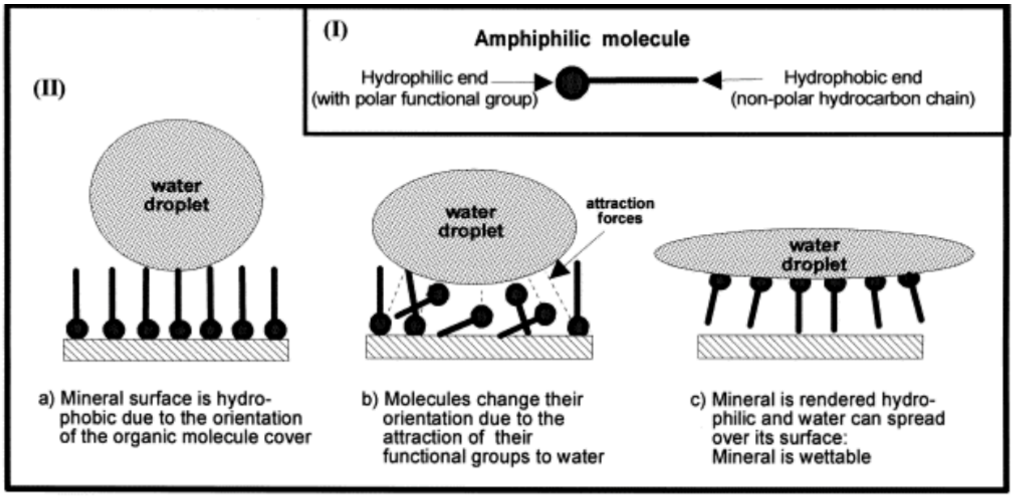

Figure 4.1- Organic compound functional group orientation impacts the ability of minerals to adsorb water (Doerr et al., 2000). This specifically demonstrates how mineral surfaces can be become hydrophilic after being hydrophobic. The non-polar ends of a amphiphilic compound are facing out from mineral surface, until moisture is presented. The compounds switch alignments so the polar end is facing the incoming moisture. This allows for water to enter the mineral surface and creates potential for cation exchange and loss of organic matter in zonal layers closer to the mineral surface.

4.2 Water Repellency

The ability of soil to absorb water is varied with some soils exhibiting water repellency, or an inability to absorb water (Doerr et al., 2000). Water repellent soils have mineral bonding patterns that contain more hydrophobic, non-polar organic compounds than polar compounds. Water repellency occurs when capillary action and cohesion, the forces holding water to soil, are blocked by a layer of organic material that acts as a barrier between water and the soil (Figure 7) (Hallett, 2007; Mao et al., 2019). Soil that is water repellent has balls of water that are formed on the soil surface instead of absorbing into soil (Figure 4.2) (Doerr et al., 2000; Adam, 1963).

Water repellency occurs in conjunction with certain soil and environmental conditions. The amount of moisture in soil is likely to change as a result of climate change. Soil moisture changing is a concern for carbon storage because there is a well-documented increase in carbon emissions if a soil comes in contact with moisture after a period of dryness (e.g. Jarvis et al., 2007; Unger et al., 2010) This is known as the Birch Effect, The Birch Effect is usually associated with topsoil and remains unclear if the Birch Effect can impact subsoil carbon storage (Birch,1958; Sanchez-Garcia et al., 2020). As water repellency can potentially increase carbon loss, moisture is an important environmental factor on carbon storage to understand.

The impact of water repellency will vary by soil mineralogy and ultimately by broad definition of soil type. It should also be noted that these factors controlling water repellency often have regional and climatic variations. Sandy soils, for example, have large grain sizes, less surface area and are considered to be more hydrophobic than other soil types (Harper et al., 2000). Arid or desert soils also demonstrate water repellency (e.g., Jaramillo et al., 2000), as minerals in these soils are hydrophobic due to the organic compounds rarely being exposed to moisture that would alter compound orientation (Figure 4.1). For example, clay soils have increased surface area that normally makes these soils less prone to hydrophobic barrier formation. Clay minerals will usually demonstrate a large capacity for mineral bonding, due to high specific surface area increasing available sites for cation exchange and organic compound bonding. As a result of more specific surface area, organic matter bonding to clay minerals lessens the risk of complete exposure of all bond compounds to moisture. In clay mineral soils organic matter directly bonded to the mineral surface will not be released as more non-polar compounds are attached to mineral surfaces and less likely to be desorbed into the soil (Feng et al., 2014). Although most carbon storage occurs in clay rich mineral soil, the presence of aluminosilicates can limit the amount of carbon stored in a soil. An excess of clay in soils (up to 23% clay content) and 13% coverage by organic content over the mineral surface, creates water repellency in clay soils by forming a hydrophobic surface barrier (Singer and Ugolini, 1976; McGhie and Posner, 1980). Clay soil is also more likely to demonstrate a non-polar preferred compound orientation (Mainwaring et al., 2013), that will likely increase water repellency as this soil may be more prone to hydrophobic barrier formation. Increased water repellency will most likely reduce the amount of carbon that can be sorped to the mineral surface through cation exchange.

On the other hand, when different minerals are present, moisture can increase carbon storage. Increased moisture has the inverse effect in soils with hydrous iron and aluminum. Moisture will cause organic matter to be released from iron and preferentially bond to aluminum (Inagaki et al., 2019), inducing a phase change. In moist hydrous iron and aluminum soils, aluminum is the dominant mineral undergoing sorption with organic matter to induce mineral bonding (Inagaki et al., 2019). However, the mechanism for how carbon sorbs to aluminum has yet to be fully described, limiting knowledge of carbon storage in soil dominated by aluminum.

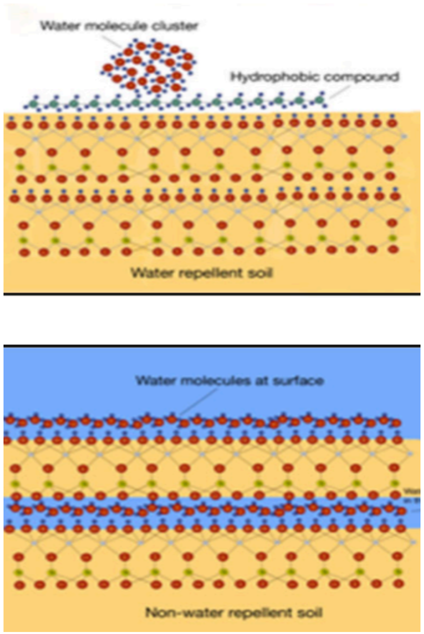

Figure 4.2 - Example of behavior of non-polar oriented organic compounds when interacting with water. Non-polar compounds force water to adhere to self and form a ball on the surface of soil (top) versus polar oriented organic compounds that spread out across the water molecule and allow for absorption into soil and adsorption onto mineral surfaces (bottom) (adapted from Mao et al.,2019).

The amount and type of carbon bound to the mineral surface can also impact water repellency. For example, soil with mineral surfaces that have high amounts of bound carbon can demonstrate water repellency as the hydrophilic oriented compounds in the kinetic zone are able to attract other functional groups that have a hydrophobic orientation (Gao et al., 2019). Although compounds with both non-polar and polar ends exist in the zonal model as portions of full compounds, the orientation of these compounds is thought to be a significant factor in soil water repellency (Gao et al., 2019). Water repellency can also alter the soil organic compounds creating changes in the chemical makeup of the soil.

For example, water repellent soils have amphiphilic compounds of 16 or more carbons; larger carbon chains than found in hydrophilic soils (Mainwaring et al., 2013; Daniel et al., 2019). Alkanes are thought to increase water repellency in soil but experimental evidence for this remains to be seen (Hallett, 2007).

The most important compounds in water repellent soil are carboxylic acid. There is some disagreement about the role of carboxylic acid in desorption of mineral bonded carbon, although carboxylic acid is needed for cation exchange. In some cases, water repellent soils have been found to have higher concentrations of long-chain carboxylic acids (Atanassova and Doerr, 2010; Mao et al., 2015; Morley et al, 2005; Horne and McIntosh, 2000; Llewellyn et al., 2004). However, some soils have also been found to have lower carboxylic acid concentrations (Inagaki et al., 2019). In water repellent soil with high amounts of carboxylic acids, cation exchange could still occur; the amount of carbon stored in the soil would likely be under normal conditions as movement of organic matter can still occur between mineral surfaces and soil. Lower carboxylic acid concentrations in water repellent soil will decrease cation exchange, reducing the amount of bonding that can occur between organic compounds and iron mineral surfaces (Inagaki et al., 2019). Therefore, carbon storage will be decrease if carboxylic acid is reduced. However, regardless of carboxylic acid concentrations, the lack of moisture to move organic matter from the root zone and topsoil also will prevent new carbon from undergoing sorption onto the mineral surfaces. Water repellency may maintain carbon already bonded onto mineral surfaces, but does not increase storage.

Chapter 5: Roots

5.1 Roots: Inputs and Storage

In addition to moisture, carbon loss is increased by the secretions of plant roots. Most subsoil carbon input is entering from surface layers after being broken down by decompositional processes, but roots create carbon that is directly input into subsoil. Input from root carbon does not require the eventual decomposition of litter from the topsoil to reach deeper layers (Rasse et al., 2005; Hicks Pries et al., 2017), and is the primary source for soil carbon in subsoil layers (Rumpel and Kogel-Knabner, 2011). For example, 50-70% of soil carbon in the boreal forest is estimated to originate from root carbon (Clemmensen et al., 2013). Subsoil carbon from roots contains various compounds from dead root cells, root exudates, and mucus (Rasse et al 2005, Heinemeyer et al., 2007; Rumpel and Kogel-Knabner, 2011). Depending on regional climatic factors, direct input of root carbon into an otherwise slow cycling carbon system has the potential to alter the balance of carbon storage in subsoil. In some soil types, carbon decomposition as a result of root exudate dramatically increased (by 380%) due to increased exposure to microbial respiration (Chen et al., 2013).

Root exudates have a large impact on carbon storage because exudates can increase microbial respiration. Glucose and amino acids are the primary compounds roots secrete, along with small amount of organic acids (Jones and

Darrah, 1994; Koo et al., 2006). These root exudates secretions attract microbes to the portion of soil immediately surrounding plant roots. The area around the roots is a zone of active microbial decomposition where breakdown of organic material and uptake of cation nutrients occurs. Secretions of root exudates allow plants to survive and uptake nutrients from soil. These root excretions will result in a decrease in soil carbon storage.

Carbon loss due to root exudates is impacted by root depth (Rumpel and Kogel-Knabner, 2011), along with varying environmental conditions. For example, shrubs may have a different impacts than trees on carbon inputs into soil, as shrubs typically have a shallower root system than a tree. Generally, roots of many plant species extend well below the 30 cm mark, with some species of trees extending meters below the topsoil and up to 70 meters in depth (Fan et al., 2017). However, plant root depth can depend on climatic conditions as well. In cold areas, the largest amount of carbon was found to be at a deeper in the shrubland soil than in forest soils (Jobbagy and Jackson, 2000). Additionally, the areas with most subsoil carbon were tropical evergreen forests (Jobbagy and Jackson, 2000), indicating that while cold climates can increase carbon associated with roots, warm climates can have the same affect depending on plant species. Research on root impact on carbon storage has produced conflicting results which vary by plant type, climate, and how deep within the soil samples were taken in relation to the plant roots.

5.2 Subsoil: Tongue and Matrix

The impact of root exudates on carbon storage depends on location within the subsoil. Subsoil is divided into root zones and matrix zones (Chabbi et al., 2009). Matrix zones are areas not affected by roots (Figure 5.1). Root zones are places of active root activity and are present in soil even after roots have decayed (Figure 5.1). In root zones, or tongues, root exudates are still chemically affecting the soil (Chabbi et al., 2009). Root zones are formed because roots extend into the same place each time as a result of decreased energy use in repeated locations of root growth (Arredondo et al., 2019). In subsoils, carbon loss most likely occurs within soil tongues (Rasse et al.,1999; Chabbi et al., 1999). Soil tongues can create spaces where microbial decomposition can occur at depth where decomposition would otherwise not be prevalent. Soil tongues may create the primary entrance for carbon in subsoils (Bundt et al., 2001).

Exudates that are secreted into the soil tongues can break apart the bonds formed between minerals and organic matter, and thereby reduce carbon storage in subsoil. The most important root exudate is a carboxylic acid known as oxalic acid. The release of oxalic acid into the soil solubilizes mineral nutrients and re-mineralizes organic matter as CO_2 (Koo et al., 2005, Keiluweit et al., 2015). Oxalic acid, more so than glucose, results in increased mineralization of carbon (Keiluweit et al., 2015). When soil was treated with either oxalic acid or glucose, it was found that oxalic acid treatments released double the CO2 than the glucose treated soils (Keiluweit et al., 2015).

5.3 Root oxalic acid and mineralogy

The magnitude of carbon loss due to root supplied oxalic acid depends on soil mineralogy. Oxalic acid impacts the soil by lowering the pH (e.g. Rukshana et al., 2011). In reactive iron minerals, low pH will result in the mobilization of iron compounds into the soil (Colombo et al., 2013). Oxalic acid exposure will remove iron cations within a mineral structure that are then replaced with aluminum (Keiluweit et al., 2015). During this replacement, iron based mineral complexes will then become more disordered as replacement occurs. The temporarily disordered mineral structure makes it difficult for new organic compounds to attach to mineral charge sites, and therefore mineral bonding is decreased (Figure 8) (Keiluweit et al., 2015). The time estimations for the mobilization vary from instantaneous to over several weeks and ensures that during the course of cation replacement, carbon is also removed from the mineral surface (Colombo et al., 2013; Keiluweit et al., 2015).

Iron mineral exposure to oxalic acid cause dissolution of the mineral and will release previously bound organic compounds into the soil (Ding et al., 2021). Iron mobilization occurs as a result of oxalic acid release because plants need iron for biological process (Colombo et al., 2013). Although previously mineral bound carbon is released from the mineral surface during iron mobilization, oxalic acid is able to be adsorbed onto the mineral structure (Keiluwiet et al., 2015). As iron cations are replaced, the carbon previously sorped onto the mineral surface remains accessible to microbes because this carbon is not able to resorb onto the aluminum mineral structure (Figure 9) (Keiluweit et al., 2015). Effectively, oxalic acid exposes organic matter to decomposition by binding to metals and clay minerals (Jones et al., 2003; Neumann and Roemheld, 2007; Keiluweit et al., 2015) and making stored carbon available for decomposition (Chabbi et al., 2009; Keiluweit et al., 2015) (Figure 5.2).The minerals that are impacted by oxalic acid secretion include crystalline minerals that contain a layer of poorly bound organic matter on the surface. Organic carbon that is not well attached to a crystalline mineral surface is subjected to root interference (Keiluweit et al., 2015). Poorly crystalline minerals as well as hydrous iron and aluminum would also be subjected to root interference. Oxalic acid in these minerals would initiate replacement of iron cations to aluminum cations. However, carbon storage on the surface of some minerals is not impacted by oxalic acid. The reduction of carbon from oxalic acid exposure does not occur on crystalline minerals where organic matter is strongly attached to the mineral surface and iron cation replacement cannot easily occur (Rasmussen et al., 2007; Keiluweit et al., 2015).

The replacement of iron cation with aluminum cations has varying impacts on carbon storage as determined by the zonal model. The weaker entropic interactions in outer layers of the zonal model would make compounds in the kinetic zone most susceptible to desorption as a result of oxalic acid exposure. The removal of the outer layer of carbon compounds would then expose compounds within the contact and hydrophobic zone to oxalic acid making these compounds vulnerable to desorption and potentially decomposition (Figure 5.2). As a result, there would be a temporary release of all compounds bound onto the mineral and carbon loss would occur.

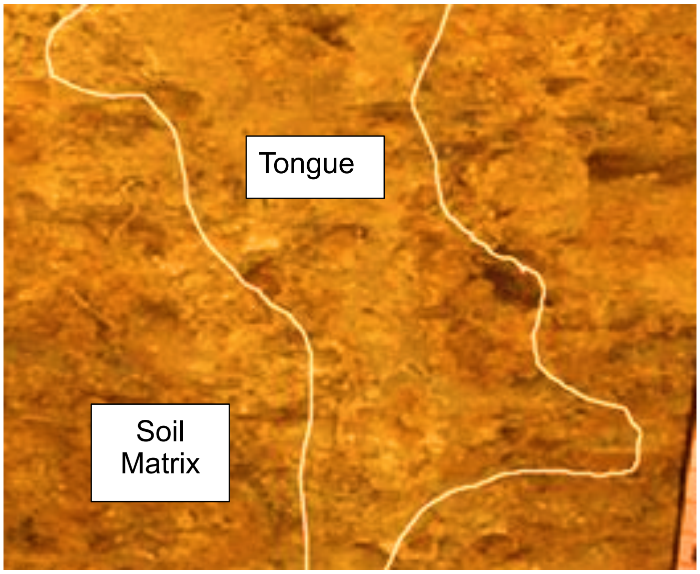

Figure 5.1- Root zones, or tongues (inside yellow line) and matrix zones (outside yellow line) in a subsoil layer (Adapted from Chabbi et al., 2009). The chemical reactions in the tongue give a visibly lighter coloration than the soil matrix.

The impact of oxalic acid on carbon storage is dependent on relative age of the soil where root growth is occurring. The loss of carbon due to oxalic acid is most likely to happen during periods of root growth in older soils, but root exudates can also increase carbon storage in younger soils (Collignon et al., 2012; Arredondo et al., 2019). Exudates and roots can induce weathering of soil parent rock. Weathering creates mineral bonds upon initial introduction to young soil but disrupts bonds if introduced to weathered, older soil (Arredondo et al., 2019). In younger soil, root exudates erode feldspars and quartz creating carbon accumulation in soil by forming organic mineral bonds between poorly crystalline iron and aluminum minerals (Arredondo et al., 2019). Root exudates also help the solidification of clay mineral structures after initial entry into the soil, thus creating the mineral structures for organic matter to bind to over long term (Arredondo et al., 2019).

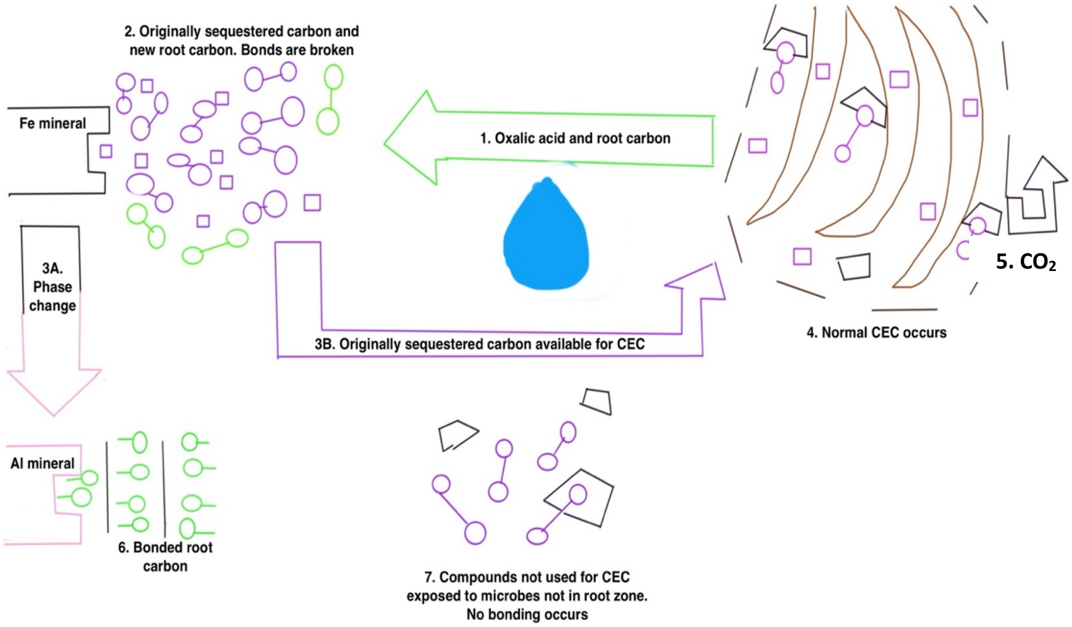

Figure 5.2- Schematic diagram of oxalic acid affecting the mineral structure and releasing organic compounds. Oxalic acid and root carbon disrupt zonal mineral bonding of currently sequestered carbon (1 and 2). Oxalic acid cause mobilization of iron into soil and aluminum replaces iron in the mineral structure (referred to as phase change on this diagram) (3A). Originally sequestered carbon is exposed to CEC processes during phase change (3B) and transported to root zone where normal CEC process can occur (4) that will emit CO_2 (5). Organic compounds not used by the plant are left outside the root zone in soil pores and in soil water (7). These compounds are exposed to microbes and do not re-bound to the mineral once a phase change from iron to aluminum has occurred. Carbon that originated from roots along with the oxalic acid secretion is bonded to aluminum minerals (6 and 7). Carbon is stored after phase change but no new carbon is added to the mineral surface for sequestration (Adapted from Keiluwiet et al., 2015).

Chapter 6: Improving carbon sampling/monitoring

This review has highlighted how conditions such as roots, moisture, and mineralogy, can impact soil mineral carbon storage. The predictability of how roots and moisture impact carbon storage, and therefore by extension how mineral bonding functions as a carbon storage process, is dependent on stable climatic conditions. The imposing threat of climate change may impact how much soil carbon stored. However, soil has the potential to become part of the solution to anthropogenic climate change if carbon storage can be increased. Soil could potentially serve as short term solution however; soil sampling must be done to account for soil carbon storage processes. Additionally, a system of monitoring plant roots and soil moisture must be developed to determine how the environmental factors that impact carbon storage are changing due to climate change.

In order to begin to increase soil carbon, soil scientists across the globe developed the goal of increasing the amount of carbon within soils by 0.04%, or by 4 per mille, in order to potential use soil to offset human emissions (Minansy et al., 2017). Using soil data from 20 regions across the globe, it was determined that an increase in soil carbon of 0.04% within the top 1 meter could result in the potential sequestration of 2-3 Pg of carbon per year (Minansy et al., 2017). This is the equivalent of a 20-30% offset in the 11 Pg carbon (40 Pg of CO_2) emitted yearly by humans (La Quere et al., 2018).

The goal of increasing soil carbon is complicated by many of inherent conditions present within the soil. First, the potential of soil to store carbon is not universal. For example, desert soil will have limited capacity for increased carbon storage due to increased water repellency that will prevent the addition of new carbon from reaching mineral surfaces. As a result, there is thought to be limited opportunity for desert soils to reach the required 0.04% carbon increases to meet storage goals (Schlesinger and Amundson, 2019). As a desert soil cover a large amount of the Earth surface, the amount of soil in which storage enhancements could be achieved is thought to be limited to forest and agriculture land (Schlesinger and Amundson, 2019). Furthermore, carbon storage is thought to not be permanent and is often reversible (Powlson et al., 2011). For example, if mineral bound organic matter is exposed to oxalic acid then stored carbon can be removed from mineral surfaces and lost to decomposition. Currently, the baseline soil carbon estimates used to produce the goal do not fully take into account how soil carbon storage may be impacted by processes that alter soil carbon loss, such as depth of roots and moisture.

Additionally, the 4 per mille goal does not provide a means by which soil carbon can be increased. The lack of methods for enhancing carbon storage is in part because soil carbon storage is dependent on understanding localized conditions, such a plant root depth. In order to begin to meet the 4 per mille goal, there must first be a determination of localized soil carbon amounts followed by a monitoring program to determine the impact of soil carbon loss processes on storage. In the United States, a basic program, the Rapid Carbon Assessment program (RaCA) was set up by the USDA and National Resource Conservation Service (NRCS) to establish initial national estimates of carbon at specific locations within the United States (Willis et al., 2014). The purpose of the RaCA was to establish soil carbon amount estimates across 6000 individual sites down to 1 meter in depth (Willis et al., 2014). The RaCA estimated carbon in soil across 17 regions within the continental United States grouped by similar climatic factors (Figure 6.1). The results of the program found most soil carbon was located within the top 5 cm of most soil, with the largest carbon amounts located within coastal wetlands when all carbon amounts where averaged together (Rapid Carbon Assessment Project, 2013).

Although the RaCA provided an estimation of the amount of carbon in specific locations, it is limited in that mineral bonding and numerous environmental factors, such as roots and moisture were not accounted for at the sampling sites. The RaCA also did not determine changes in carbon amounts over long periods of time as the program was a single year study. In order to determine how to increase soil carbon, soil carbon sampling must change to account for the factors that impact carbon storage. For example, sampling must take into account land use changes on the sampling site if the scale of human impact on soil is to be accounted for in carbon estimates (e.g. Zaehle et al., 2007). Current estimates also do not account for historic or current changes in land use, such as city growth or afforestation (Minasny et al., 2017). However, the main change to soil carbon sampling must be the depth to which sampling occurs.

The RaCA estimates of carbon extend to a 1 meter depth, but the reliance on a universal sampling depth limit is not useful for determining baseline carbon amounts measurements. Soil carbon sampling will ultimately need to exceed 1 meter because of the of the wide range of climates and land uses within the US results in large variations in plants and root depths. Sampling must occur down to the lowest depths at which roots are present as roots exudates are a large controlling mechanism for soil carbon storage. For example, within colder and permafrost soils, soil with roots had over 1.5 times the amount of carbon lost from root soil than from soil with little roots (Keuper et al., 2020). As a result, 1 meter may not be an adequate sampling depth to develop an accurate estimation of the amount of soil carbon; especially as root depth in some climates is predicted to deepen past 1 meter by 2100 (Keuper et al., 2020).

Sampling may not be able to be done uniformly across the entirety of the US. Sampling should ultimately be region specific and in concurrence with changes in land, vegetation, and climatic conditions. In the subsoil, the slow rate of carbon accumulation in subsoils makes estimating changes in soil carbon difficult to establish on current 3-5 year sampling cycles. Therefore, sampling must be undertaken with relative frequency (Post et al., 2001), and not just every 3-5 years. While recognizing that extensive soil sampling costs is expensive, sampling should occur at a depth that accounts for all factors that impact carbon storage, such as the depth of roots and reach of soil water. In addition to changing the depth to which soil carbon sampling occurs, a carbon monitoring program needs to be developed to determine carbon loss due to environmental factors. Many countries, such as Denmark and France have national carbon monitoring systems in place (e.g. Tashizaden-Toosi et al., 2014; King et al., 2017), however the extensive size and wide range of environments within the US would make the development of a national monitoring system difficult. In order to account for climatic and geographical variance, a monitoring system may be broken into 17 parts based on the regions developed in the RaCA (Figure 6.1). The use of these regions would group soil sampling and any solutions to enhancing carbon storage by similar climates. A carbon monitoring system that monitors soil carbon amounts below 1 meter in depth would be useful, as monitoring carbon loss from the subsoil would give greater accuracy to carbon estimates and how climate change alters these estimates. In a large nation, carbon monitoring will depend on sampling that takes into account soil carbon at both the topsoil and subsoil layers as well as environmental factors that influence carbon input and loss. Monitoring systems must involve direct sampling of soil carbon on-site and not rely only on computer modeling to determine how soil carbon changes (Bradford et al., 2016). The potential of soil carbon storage to help offset human carbon emissions (when combined with reduction in those emissions) makes a monitoring system worth developing. In order to develop a monitoring system, it is necessary to first develop experiments that could serve as the basis for a long term monitoring system. However, monitoring is expensive and can be impacted by complex and often interacting environmental factors. In order to take cost into account, a monitoring system should focus on mineral content and plant roots in two environments where environmental conditions are most varied. A study conducted in a forest and prairie environment, would compare oxalic acid concentrations in both environments. The comparisons of concentrations of oxalic acid would determine the carbon amounts in parts of the soil impacted by oxalic acid. Furthermore, a comparison of oxalic acid concentrations in the soil tongue and soil matrix is needed to understand soil carbon storage. This is particularly important at depth, where oxalic acid is most likely to reduce carbon storage. Ideally, this study would show that because trees have deeper root depths than prairie shrubs, there is greater reduction in carbon amounts at depth in the soil tongues of forests than prairie shrubs. Oxalic acid concentrations would also be higher in forest environments due to the increased amount of roots in forests. Prairies would likely have less carbon loss at depth and would be less impacted by oxalic acid induced carbon losses.

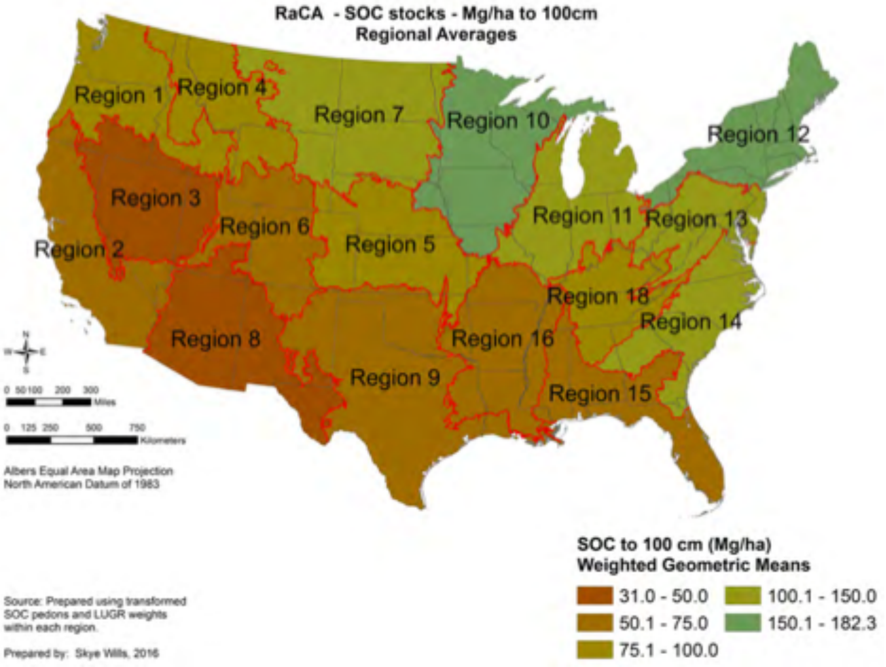

Figure 6.1- Rapid Carbon Assessment estimation of carbon amounts down to 1 meter (100 cm) over 17 regions. Regions have a similar climatic grouping (USDA-NRCS, 2016).

A comparison study of oxalic acid in different environments will compare the amount of oxalic acid excretions and carbon amounts in soil across temperate forest and prairie/field environments in the United States. The experiment will use soil samples taken below 1 meter and preferably to the lowest limit of roots as determined by the plant species with the deepest root depths. At a minimum soil sampling should occur to at least 3 meters in depth. Samples should be taken both in the soil tongue and soil matrix every 30 centimeters between 1 and 3 meters, occurring around a plant with the deepest roots in the respective environment. Samples should be tested for oxalic concentrations and amount of organic matter in both soil tongue and matrix between 1 and 3 meters. Oxalic acid in soil is most commonly measured using high performance liquid chromatography (Zhang et al., 2018). Organic matter amounts will be studied through NMR. Samples should be taken every month, as carbon loss due to oxalic acid secretion is thought to occur within a couple weeks of initial exposure. Monthly sampling will allow for a determination of how amounts of organic matter are changing at depth and over time.

As a result of this study, it would be possible to conclude that any carbon increasing efforts would focus on prairie soils. These soils will have less change in carbon amounts and are less impacted by oxalic acid at depth, due to less roots. This study would set up the basis of studies that need to be performed to begin a monitoring system that monitors both environmental conditions and carbon amounts changes in soil.

Chapter 7: Summary

Soil can be a potential solution to climate change. Soil can store several times the amount of carbon currently in the atmosphere. In order to fully take advantage of soil carbon storage, the chemistry of soil must be understood. Primarily, soil carbon storage is not equal across all soil depths. Most soil carbon is stored in subsoil, where the carbon is less likely to be lost to the atmosphere via microbial decomposition or erosion. Carbon is stored in subsoil due to a chemical process known as mineral bonding. Mineral bonding is a complex process where organic matter attaches to mineral surfaces. In subsoil, mineral bonding occurs mainly on the surface of clay minerals and iron hydroxides. Organic matter is stored through layered attachment onto a mineral surface. The layered attachment on mineral surface allows large amounts of carbon to be maintained in soil for long periods.

Soil carbon storage is a dynamic process where the amount of carbon stored through mineral bonding is dependent on the environmental conditions in a soil, such as moisture and plant roots. Moisture moves organic matter from the soil to the mineral surface allowing more mineral bonding to occur. However, water also removes organic matter from the soil during cation exchange processes, where by the exposure of organic matter in the outer layers of carbon is removed from the mineral surface. Plant roots also contribute to carbon loss through the secretion of root exudates.

The most important exudate is oxalic acid, which can cause dissolution of iron hydroxides and the release of all organic matter. Exposure of mineral bonded carbon to oxalic acid is a major contributor to carbon loss from subsoil.

The impact of roots and moisture in soil carbon storage must be considered when determining how to increase carbon storage, as both roots and moisture can cause significant loss of soil carbon and disrupt carbon storage enhancement efforts. In order to begin to accomplish the goal of increasing soil carbon in the United States, it is necessary to first determine baseline carbon amounts that take into account carbon at different depths. Any carbon increases in soil will be dependent on the climatic conditions that change the amount of soil carbon stored. As such, carbon estimates need to be in concurrence with environmental factors, such as sampling carbon to the deepest possible depth of roots to fully account for carbon potentially lost through dissolution of mineral bonds by oxalic acid.

Long term monitoring efforts of carbon must also take place to determine how environmental conditions impact carbon storage. For example, a monitoring system could begin with determining carbon amounts and oxalic acid concentrations in forest and prairie soils. Due to shallower root depths, prairie soils may store more carbon as oxalic acid exposure is not dissolving mineral bonds at depth. As a result, focusing any soil carbon enhancements efforts on prairies soils may be more productive for decreasing human carbon emissions than enhancement efforts in forest soils. In soil science, carbon sequestration in soil is often considered to be one of many potential solutions to climate change. If soil carbon can be increased there is potential to offset human carbon emissions over the next few decades. However, to effectively use soil for carbon storage will require altering how carbon sampling is done, frequent sampling to account for changing environmental conditions, and a vigorous monitoring system using carbon data collected from soil at depth.

References

Adam, N.K. (1963). *Principles of water-repellency*. J.L. Moillet (Ed.), Water Proofing and Water-Repellency, Elsevier, London (1963), pp. 1-23

Andong, C., Feng, W., Zhang, W., & Xu, M. (2016). Climate, soil texture, and soil types affect the contributions of fine-fraction-stabilized carbon to total soil organic carbon in different land uses across China. *Journal of Environmental Management*. 172. pgs. 2-9. ISSN 0301-4797.

Angst, G. , Messinger, Greiner, J. M., Häusler, W., Hertel, D., Kirfel,K., Kögel-Knabner, I., Leuschner, C., Rethemeyer, J., & Mueller, C.W. (2018). Soil organic carbon stocks in topsoil and subsoil controlled by parent material, carbon input in the rhizosphere, and microbial-derived compounds. *Soil Biology and Biochemistry*. 122:19-30. ISSN 0038-0717.

Araujo, M.A., Zinn, Y.L., & Lal, R. (2017). Soil parent material, texture and oxide contents have Little effect on soil organic carbon retention in tropical highlands. Geoderma. Vol 300,Pgs. 1-10. ISSN 0016-7061,

Archer, D. (2012). Carbon on Earth. In: Global Warming: Understanding the Forecast. Wiley Publishing. 2nd edition. ISBN-0470943416.

Arnarson, T.S., & Keil R.G. (2001). Organic-mineral interactions in marine sediments studied using density fractionation and X-ray photoelectron spectroscopy. *Org. Geochem* 32:1401–1415.

Arredondo, M.G., Lawrence, C.R., Schulz, M.S., Tfaily, M.M., Kukkadapu, R., Jones, M.E., Boye, K., & Keiluweit, M. (2019). Root-driven weathering impacts on mineral-organic associations in deep soils over pedogenic time scales. *Geochimica et Cosmochimica Acta*, 263. Pgs. 68-84. ISSN 0016-7037.

Arrouays, D., Deslais, W. and Badeau, V. (2001), The carbon content of topsoil and its geographical distribution in France. Soil Use and Management, 17: 7-11.

Atanassova, I., & Doerr, S. (2010). Organic compounds of different extractability in total solvent extracts from soils of contrasting water repellency. *European Journal of Soil Sci*ence., 61 (2) pp. 298-313

Batjes, N.H. (1996). Total carbon and nitrogen in the soils of the world. *European Journal of Soil Science*, 47. pp. 151-163

Batjes, N. (2014). Total carbon and nitrogen in the soils of the world (EJSS Land Mark Paper No. 3). *European Journal of Soil Science*. 47. 151-163.

Balesdent, J., & Mariotti, A. (1996). *Measurement of soil organic matter turnover using t3C natural abundance.* In: Boutton, T.W., Yamasaki, S. (Eds.), Mass Spectrometry of Soils. Marcel Dekker, New York, pp. 83-112.

Balesdent, J., Basile-Doelsch, I., Chadoeuf, J. Cornu, S., Derrien, d., Fekiacova, Z., & Hatte, C. (2018). Atmosphere–soil carbon transfer as a function of soil depth. *Nature* **559,** 599–602.

Birch, H.F. (1958). The effect of soil drying on humus decomposition and nitrogen availability. *Plant Soil*, 10. pp. 9-31.

Bradford, M.A., Wieder, W.R., Bonan, G.B., Fierer, N., Raymond, P.A., & Crowther, T.W. (2016). Managing uncertainty in soil carbon feedbacks to climate change. *Nature Clim Change* **6,** 751–758 (2016).

Bundt, M., Widmer, F., Pesaro, M., Zeyer, J., & Blaser, P. (2001). Preferential flow paths: biological 'hot spots' in soils. *Soil Biology & Biochemistry*, 33. pp. 729-738

Chabbi, A., Kögel-Knabner, I., & Rumpel, C. (2009). Stabilised carbon in subsoil horizons is located in spatially distinct parts of the soil profile. *Soil Biol Biochem* 41:256–271

Chapman, H. (1965). *Cation-Exchange Capacity*. Methods of Soil Analysis, A.G. Norman (Ed).

Chappell, A., Baldock, J. & Sanderman, J. (2016). The global significance of omitting soil erosion from soil organic carbon cycling schemes. *Nature Clim Change* **6,** 187–191 https://doi.org/10.1038/nclimate2829

Chassin, P. (1979) Hypothèse sur la structure du complexe argilo-humique. Conséquences sur les processus d'humification. *Science du Sol*. 4:323–332

Chen, S., Huang, Y., Zou, J., & Shi, Y. (2013). Mean residence time of global topsoil carbon depends on temperature, precipitation and soil nitrogen. *Global and Planetary Change* 100, 99–108.

Christensen, B.T.(1996). *Carbon in primary and secondary organomineral complexe*s. In: Carter, M.R., Stewart, B.A. (Eds.), Structure and Organic Matter Storage in Agricultural Soils. Advances in Soil Science, CRC Lewis Publishers, Boca Raton, pp. 97-165.

Clemmensen, K., Bahr, A., Ovaskainen, O., Dahlberg, A., Ekblad, A., Wallander, H., Stenlid, J., Finlay, R., Wardle, D., &Lindahl, B.D. (2013). Roots and associated fungi drive long-term carbon sequestration in boreal forest. *Science* **339,** 1615–1618.

Collignon, C., Ranger, J. & Turpault, M. P. (2012). Seasonal dynamics of Al- and Fe-bearing secondary minerals in an acid forest soil: Influence of Norway spruce roots (*Picea abies* (L.) Karst.). *Eur. J. Soil Sci.* 63**,** 592–602.

Condron, L., Stark, C., O'Callaghan, M., Clinton, P., & Huang, Z. (2010) The Role of Microbial Communities in the Formation and Decomposition of Soil Organic Matter. In: Dixon G.,Tilston E. (eds) Soil Microbiology and Sustainable Crop Production. Springer, Dordrecht. https://doi.org/10.1007/978-90-481-9479-7_4

Colombo, C., Palumbo, G., He, J-Z., Pinton, R., &Cesco, S. (2013). Review on iron availability in soil: interaction of Fe minerals, plants, and microbes. *J. Soils Sediments*. 14:538–548

Culman, S., Mann, M., & Brown, C. (2019). *Calculating Cation Exchange Capacity, Base Saturation, and Calcium Saturation.* Agriculture and Natural Resources. Ohio State University Extension. ANR-81.

Daniel, S.M., Nicholas, R.R., Uddin, M., Harper, R.J., & Henry, D.J. (2019). Soil water repellency: A molecular-level perspective of a global environmental phenomenon,. *Geoderma.* 338. Pgs. 56-66. ISSN 0016-7061.

Ding, Y., Ye, Q., Liu, M., Shi, Z., & Liang, Y. (2021). Reductive release of Fe mineral-associated organic matter accelerated by oxalic acid. Science of The Total Environment. Vol. 763,142937. ISSN 0048-9697.

Doerr, S,H., Shakesby, R.A., & Walsh, R.P.D. (2000). Soil water repellency: its causes, characteristics and hydro-geomorphological significance. *Earth Sci. Rev.*, 51, pp. 33-65

Eusterhues, K., Rumpel, C., & Kogel-Knabner, I. (2005). Organo-mineral associations in sandy acid forest soils: importance of specific surface area, iron oxides and micropores. *European Journal of Soil Science,* 56: 753-763.

Falkowski, P., Scholes, R. J., Boyle, E., Canadell, J., Canfield, D., Elser, J., Gruber, N., Hibbard, K., Hogberg, P., Linder, S., Mackenzie, F. T., Moore, B., Pedersen, T., Rosental, Y., Seitzinger, S., Smetacek, V., & Steffen, W. (2000). The global carbon cycle: A test of our knowledge of earth as a system. *Science*, *290*(5490), 291–296.

Fan, Y., Miguez-Macho, G., Jobbágy, E.G., Jackson, R.B.,& Otero-Casal, C. (2017). Hydrologic regulation of plant rooting depth. *Proc. Nat. Acad. Of Sci.* vol. 114: 40 10572-10577. ISSN: 1091-6490

Feng, X., Simpson, A.J., Simpson, M.J. (2005). Chemical and mineralogical controls on humic acid sorption to clay mineral surfaces. *Organic Geochemistry*. 36:11. Pgs. 1553-1566, ISSN 0146-6380.

Feng, W., Plante, A.F., Aufdenkampe, A.K.,& Six, J. (2014). Soil organic matter stability in organo-mineral complexes as a function of increasing C loading. *Soil Biology and Biochemistry*. Vol. 69. Pgs 398-405. ISSN 0038-0717.

Fierer, N, Allen, A.S., Schimel, J.P., Holden, P.A. (2003). Controls on microbial CO2 production: a comparison of surface and subsurface soil horizons. *Glob Change Biol* 9:1322–1332

Gao, J., Jansen, B., Cerli, C., Helmus, R., Mikutta, R., Dultz, S., Guggenberger, G., & Kalbitz, K. (2017). Competition and surface conditioning alter the adsorption of phenolic and amino acids on soil minerals. *Eur. J. Soil Sci.* **68**, 667– 677.

Gao, J., Jansen, B., Cerli, C., Helmus, R., Mikutta, R., Dultz, S., Guggenberger, G., Vogel, C., & Kalbitz, K. (2018). Organic matter coatings of soil minerals affect adsorptive interactions with phenolic and amino acids. *Eur. J. Soil Sci.* **69**, 613–624.

Gao, J., Mikutta, R., Jansen, B., Guggenberger, G., Vogel, C. and Kalbitz, K. (2019). The multilayer model of soil mineral–organic interfaces—a review . *J. Plant Nutr. Soil Sci.,* 183: 27-41.

Gartzia-Bengoetxea, N., Virto, I., Arias-Gonzalez, A., Enrique, A., Fernandez-Ugalde, O., & Barre, P. (2020). Mineral control of organic carbon storage in acid temperate forest soils in the Basque Country. *Geoderma.* Vol. 358,113998. ISSN 0016-7061,

Gu, B., Schmitt, J., Chen, Z., Llang, L., &McCarthy, J.F. (1994). Adsorption and Desorption of Natural Organic Matter on Iron Oxide: Mechanisms and Models. Environ. Sci. Technol. 1994, 28, 38-46.

Guggenberger, G., Zech, W., & Schulten, H-R. (1994). Formation and mobilization pathways of dissolved organic matter: evidence from chemical structural studies of organic matter fractions in acid forest floor solutions. *Organic Geochemistry*, 21:1,Pgs. 51-66. ISSN 0146-6380.

Guo, L.B., & Gifford, R.M .(2002). Soil carbon stocks and land use change: a meta-analysis. *Global Change Biol* 8:345–360

Hallett, P.D. (2007). *An introduction to soil water repellency* In: Proceedings of the 8th International Symposium on Adjuvants for Agrochemicals (ISAA2007), Columbus, USA

Harrison, R.B., Footen, P.W., Strahm, B.D. (2011). Deep Soil Horizons: Contribution and Importance to Soil Carbon Pools and in Assessing Whole-Ecosystem Response to Management and Global Change, *Forest Science*, 57:1. Pages 67–76,

Harper, R.,J., McKissock, I., Gilkes, R.J., Carter, D.J., & P.S. Blackwell, P.S. (2000). A multivariate framework for interpreting the effects of soil properties, soil management and land-use on water repellency. *J. Hydrol*., 231–232. pp. 371-383

Hawken, P. (2017). *Drawdown*: *The Most Comprehensive Ever Proposed to Reduce Climate Change.* New York, New York: Penguin Books.

Heinemeyer, A., Hartley, I.P., Evans, S.P., Carreira De la Fuente, J.A. & Ineson, P. (2007). Forest soil CO_2 flux: uncovering the contribution and environmental responses of ectomycorrhizas. *Global Change Biology*, 13: 1786-1797.

Hicks Pries., C.E., Bird, J.A., Castanha, C. Hatton, J-P., Torn, M.S. (2017). Long term decomposition: the influence of litter type and soil horizon on retention of plant carbon and nitrogen in soils. *Biogeochemistry* **134,** 5–16.

Horne, D.J., & J.C. McIntosh. (2000). Hydrophobic compounds in sands in New Zealand —extraction, characterisation and proposed mechanisms for repellency expression. *J. Hydrol.,* 231–232. pp. 35-46

Inagaki, T. M., Possinger, A. R., Grant, K. E., Schweizer, S. A., Mueller, C. W., Derry, L. A., Lehmann, J., & Kogel-Knaber, I. (2020). Subsoil organo-mineral associations under contrasting climate conditions. *Geochim. Cosmochim. Acta* 270, 244–263.

Jackson, M.L. (1963). Aluminum Bonding in Soils: a Unifying Principle in Soil Science. *Soil Science Society of America Journal.* 27: -10.

Jaramillo, D.F., Dekker, L.W., Sistema, C.J., & Hendrickx., J.M.H. (2000). Occurrence of soil water repellency in arid and humid climates. *J. Hydrol*., 231–232, pp. 105-111

Jarvis, P., Rey, A., Petsikos, C., Wingate, L., Rayment, M., Pereira, J., Banza, J., David, J., Miglietta, F., Borghetti, M., Manca, G., & Valentini, R. (2007). Drying and wetting of Mediterranean soils stimulates decomposition and carbon dioxide emission: the "Birch effect", *Tree Physiology*, Vol. 27:7. Pages 929–940.

Jobbágy, E. G., & Jackson, R. B. (2000). The vertical distribution of soil organic carbon and its relation to climate and vegetation. *Ecol. Applic.* 10, 423–436.

Jones, D.L., Darrah, P.R. (1994). Amino-acid influx at the soil-root interface of *Zea mays* L. and its implications in the rhizosphere. *Plant Soil* **163,** 1–12.

Jones, D. L., Dennis, P. G. & vanHees, P. A. W. (2003). Organic acid behavior in soils—misconceptions and knowledge gaps. *Plant Soil* **248,** 31–41.

Jones, E., Singh, B. (2014). Organo-mineral interactions in contrasting soils under natural vegetation. *Frontiers in Environmental Science*. Vol. 2.

Kaiser, K., Guggenberger, G., Haumaier, L. and Zech, W. (1997). Dissolved organic matter sorption on sub soils and minerals studied by ^{13}C-NMR and DRIFT spectroscopy. European Journal of Soil Science, 48: 301-310.

Kaiser, K., & Kalbitz,K. (2012). Cycling downwards – dissolved organic matter in soils *Soil Biology and Biochemistry*, 52, pp. 29-32

Kalbitz, K., Schwesig, D., Schmerwitz, J., Kaiser, K., Haumaier, L., Glaser, B., Ellerbrock, R., & Leinweber, P. (2003). Changes in properties of soil-derived dissolved organic matter induced by biodegradation. *Soil Biology & Biochemistry*, **35**, 1129– 1142.

Kalbitz, K., & Kaiser, K. (2008). Contribution of dissolved organic matter to carbon storage in forest mineral soils. *Journal of Plant Nutrition and Soil Science*, 171, pp. 52-60

Keiluweit, M., Bougoure, J.J., Nico, P.S., Pett-Ridge, J., Weber, P.K., & Kleber, M. (2015). Mineral protection of soil carbon counteracted by root exudates. *Nature Clim Change* **5,** 588–595.

Keuper, F., Wild, B., Kummu, M., Beer, C., Blume-Werry, G., Fontaine, S., Gavazov, K., Gentsch, N., Guggenberger, G., Hugelius, G., Jalava, M., Koven, C., Krab, E., Kuhry, P., Monteux, S., Richter, A., Shahzad, T., Weedon, J.T., & Dorrepaal, E. (2020). Carbon loss from northern circumpolar permafrost soils amplified by rhizosphere priming. *Nat. Geosci.* **13,** 560–565.

Kindler, R., Siemens, J., Kaiser, K., Walmsley, D.C., Bernhofer, C., Buchmann, N., Cellier, P., Eugster, W., Gleixner, G., Grunwald, T., Heim, A., Ibrom, A., Jones, S.K., Jones, M., Klump, K., Kutsch, W., Larson, K.S., Lehuger, S., Loubet, B., Mckenzie, R., Moors, E., Osborne, B., Pilegaard, K., Rebmann., C., Saunders, M., Schmidt, M.I.W., Schrumpf, M., Seyfferth, J., Skiba, U., Saussana, J-F., Sutton, M.A., Tefs, C., Vowinckel, B., Zeeman, M.J., & Kaupenjohann, M., (2011). Dissolved carbon leaching from soil is a crucial component of the net ecosystem carbon balance. *Global Change Biol*ogy, 17. pp. 1167-1185

King, D., Stengel, P., Jamagne, M., Le Bas, C., & Arrouays, D. (2017). Soil Mapping and Soil Monitoring: State of Progress and Use in France. European Soil Bureau. Research Report 9.

Kleber, M., Sollins, P., & R. Sutton, R. (2007). A conceptual model of organo-mineral interactions in soils: self-assembly of organic molecular fragments into zonal structures on mineral surfaces. *Biogeochemistry*, 85 (1). pp. 9-24

Kleber, M., Eusterhues,K., Keiluweit, M., Mikutta, C., Mikutta, R., & Nico, P.S. (2015). Chapter One - Mineral–Organic Associations: Formation, Properties, and Relevance in Soil Environments. *Advances in Agronomy*. Academic Press. 130. Pg 1-140. ISSN 0065-2113. ISBN 9780128021378.

Kogel-Knaber, I. (1997). 13C and 15N NMR spectroscopy as a tool in soil organic matter studies. *Geoderma.* 80. 243-270.

Koo, B-J., Chang, A.C., Crowley, D.E., & Page, A.L. (2006). Characterization of Organic Acids Recovered from Rhizosphere of Corn Grown on Biosolids-Treated Medium,Communications in Soil Science and Plant Analysis, 37:5-6, 871-887.

Kravchenko, A., Otten, W., Garnier, P., Pot, V. & Baveye, P.C. (2019). Soil aggregates as biogeochemical reactors: Not a way forward in the research on soil–atmosphere exchange of greenhouse gases. *Glob Change Biol*, 25: 2205-2208.

Kreyling, O., Kölbl, A., Spielvogel, S., Rennert, T., Kaiser, K. and Kögel-Knabner, I. (2013). Density fractionation of organic matter in dolomite-derived soils. Z. Pflanzenernähr. *Bodenk*., 176: 509-519.

Leppalammi-Kujanssuu, J., Aro, L., Salemaa, M., Hansson, K., Kleja, D.B., & Helmisaari, H-S. (2014). Fine root longevity and carbon input into soil from below- and aboveground litter in climatically contrasting forests. *Forest Ecology and Management.* Vol. 326. Pgs 79-90. ISSN 0378-1127.

Le Quéré, C., Andrew, R. M., Friedlingstein, P., Sitch, S., Hauck, J., Pongratz, J., Pickers, P. A., Korsbakken, J. I., Peters, G. P., Canadell, J. G., Arneth, A., Arora, V. K., Barbero, L., Bastos, A., Bopp, L., Chevallier, F., Chini, L. P., Ciais, P., Doney, S. C., & Zheng, B. (2018). Global Carbon Budget 2018. *Earth System Science Data*, *10*(4), 2141–2194.

Liu, S.Y., Kleber, M., Takahashi, L.K., Nico, P., Keiluweit, M., &Ahmed, M. (2013). Synchrotron-Based Mass Spectrometry to Investigate the Molecular Properties of Mineral–Organic Associations. *Anal. Chem.* 2013, 85, 12, 6100–6106.

Llewellyn, C.T., Doerr, S.H., Douglas, P., Morley, C.P.,& Mainwaring, K.A. (2004). Soxhlet extraction of organic compounds associated with soil water repellency *Environ. Chem. Lett*., 2 (1), pp. 41-44

Lorenz K., & Lal, R. (2018). Soil Carbon Stock. In: *Carbon Sequestration in Agricultural Ecosystems.* Springer, Cham. https://doi.org/10.1007/978-3-319-92318-5_2

Lützow, M.V., Kögel-Knabner, I., Ekschmitt, K., Matzner, E., Guggenberger, G., Marschner, B. and Flessa, H. (2006). Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions – a review. *European Journal of Soil Science*, 57: 426-445

Macht, F., Eusterhues, K., Pronk, G.J., Totsche, K.U. (2011). Specific surface area of clay minerals: Comparison between atomic force microscopy measurements and bulk-gas (N2) and -liquid (EGME) adsorption methods. *Applied Clay Scienc*e. 53:1. (2011). Pg. 20-26.ISSN 0169-1317

Mainwaring, K., Hallin, Douglas, I.L., Doerr, P., & Morley, C.P. (2013). The role of naturally occurring organic compounds in causing soil water repellency. *Eur. J. Soil Sci*., 64 (5) (2013), pp. 667-680

Mao, J., Nierop, K.G.J., Rietkerk, M., & Dekker, S.C. (2015).Predicting soil water repellency using hydrophobic organic compounds and their vegetation origin. Soil, 1 (1) (2015), pp. 411-425

Mao, J., Nierop, K.G.J., Dekker, S.C. Dekker, L. (2019). Understanding the mechanisms of soil water repellency from nanoscale to ecosystem scale: a review. *J Soils Sediments* 19:1 171–185

Marschner, B. & Kalbitz, K. (2003). Controls of bioavailability and biodegradability of dissolved organic matter in soils. *Geoderma*, **113**, 211–235

Mayer, L.M. (1994). Relationships between mineral surfaces and organic carbon concentrations in soils and sediments. *Chem. Geol*. 114:347–363

Mccarthy, J. (2005). Carbon fluxes in soil: long-term sequestration in deeper soil horizons. *Journal of Geo. Sci*. 15:2. Pg. 149-154.

McGhie, D.A., &Posner, A.M. (1980). Water repellence of a heavy-textured Western Australian surface soil. *Aust. J. Soil Res*., 18, pp. 309-323

Menon, M., Jia, X., Lair, G.J., P.H. Faraj, A. Blaud. (2015). Analysing the impact of compaction of soil aggregates using X-ray microtomography and water flow simulations. *Soil and Tillage Research.* Vol.150. pgs. 147-157. ISSN 0167-1987

Minasny, B., Malone, B.P., A.B. McBratney, D.A. Angers, D. Arrouays, A. Chambers, V. Chaplot, Z.-S. Chen, K. Cheng, B.S. Das, D.J. Field, A. Gimona, C.B. Hedley, S.Y. Hong, B. Mandal, B.P. Marchant, M. Martin, B.G. McConkey, V.L. Mulder, S. O'Rourke, A.C. Richer-de- Forges, I. Odeh, J. Padarian, K. Paustian, G. Pan, L. Poggio, I. Savin, V. Stolbovoy, U. Stockmann, Y. Sulaeman, C.-C. Tsui, T.-G. Vågen, B. van Wesemael, & L. Winowiecki. (2017). Soil carbon 4 per mille. *Geoderma*, 292. pp. 59-86,

Mitchell, P.J., Simpson, A.J., Soong, R., & Simpson, M.J. (2018). Nuclear Magnetic Resonance Analysis of Changes in Dissolved Organic Matter Composition with Successive Layering on Clay Mineral Surfaces. *Soil Systems*. 2(1):8.

Morley, C.P., Mainwaring, K.A., Doerr, S.H., P.Douglas, Llewellyn, C.T., & Dekker, L.W. (2005). Organic compounds at different depths in a sandy soil and their role in water repellency. *Aust. J. Soil Re*s., 43 (3) (2005), pp. 239-249

Moore, T. R.; Dalva, M. (2001). Some controls on the release of dissolved organic carbon by plant tissues and soils. *Soil Science*. 166: 1 - p 38-47.

Mustafa, A., Minggang, X., Atizaz, S., Shah, A., Abrar, M.M., Nan, S., Baoren, W., Zejiang, C., Saeed, Q., Naveed, M., Mehmood, K., & Núñez-Delgado, A. (2020). Soil aggregation and soil aggregate stability regulate organic carbon and nitrogen storage in a red soil of southern China. *Journal of Environmental Managem*ent. Vol. 270,110894. ISSN 0301-4797.

Newcomb, C.J., Qafoku, N.P., Grate, J.W., Bailey, V.L., & Yoreo, J.J. (2017). Developing a molecular picture of soil organic matter–mineral interactions by quantifying organo–mineral binding. *Nat Commun.* **8,** 396.

Neumann, G. & Roemheld, V. (2007). *The Rhizosphere: Biochemistry and Organic Substances at the Soil-Plant Interface.* CRC Press.

Oades, J.M., & Waters, A.G. (1991). Aggregate hierarchy in soils. *Soil Research* **29**, 815-828.

Oelkers, E.H., & Cole, D.R. (2008). Carbon Dioxide Sequestration A Solution to a Global Problem. *Elements*; 4 (5): 305–310.

Peixoto, L., Elsgaard, L., Rasmussen, J., Kuzyakov, Y., Banfield, C.C., Dippold, M.A., Olesen, J.E. (2020). Decreased rhizodeposition, but increased microbial carbon stabilization with soil depth down to 3.6 m. *Soil Biology and Biochemistry*. Vol. 150. 108008. ISSN 0038-0717.

Poirier, V.; Basile-Doelsch, I.; Balesdent, J.; Borschneck, D.; Whalen, J.K.; Angers, D.A. (2020). Organo-Mineral Interactions Are More Important for Organic Matter Retention in Subsoil Than Topsoil. *Soil Syst. 4*, 4.

Possinger, A.R., Bailey, S.W., Inagaki, T.M., Kögel-Knabner, I., Dynes, J.J., Arthur, Z.A., & Lehmann, J. (2020). Organo-mineral interactions and soil carbon mineralizability with variable saturation cycle frequency. *Geoderma*, 375. 114483. ISSN 0016-7061.

Post W.M., Izaurralde R.C., Mann L.K., Bliss N. (2001) Monitoring and Verifying Changes of Organic Carbon in Soil. In: Rosenberg N.J., Izaurralde R.C. (eds) Storing Carbon in Agricultural Soils: A Multi-Purpose Environmental Strategy. Springer, Dordrecht.

Powlson, D.S., Whitmore, A.P., & K.W.T. Goulding, K.W.T. (2011). Soil carbon sequestration to mitigate climate change: a critical re-examination to identify the true and the false. *Eur. J. Soil Sci.*, 62. pp. 42-55

Preston, C. (1996). Applications of NMR to soil organic matter analysis: history and prospects. *Soil Science*. 161:3. p 144-166.

Rasmussen, C., Southard, R.J. and Horwath, W.R. (2007), Soil Mineralogy Affects Conifer Forest Soil Carbon Source Utilization and Microbial Priming. Soil Sci. Soc. Am. J., 71: 1141-1150

Rasmussen, C., Southard, R.J. & Horwath, W.R. (2008), Litter type and soil minerals control temperate forest soil carbon response to climate change. Global Change Biology, 14: 2064-2080.

Rasse, D.P., Smucker, A.J.M.,& Schabenberger, O. (1999). Modifications of soil nitrogen pools in response to alfalfa root systems and shoot mulch. *Agronomy Journal*, 91, pp. 471-477

Rasse, D.P., Rumpel, C., & Dignac, M-F. (2005). Is soil carbon mostly root carbon? Mechanisms for a specific stabilisation. *Plant Soil* 269:341–356

Robertson, G. P. (2014). Soil Greenhouse Gas Emissions and Their Mitigation. *Encyclopedia of Agriculture and Food Systems*, 185–196.

Rukshana, F., Butterly, C.R., Baldock, J.A., & Tang, C. (2011). Model organic compounds differ in their effects on pH changes of two soils differing in initial pH. *Biol Fertil Soils* **47,** 51–62 .

Rumpel, C., & Kögel-Knabner, I. (2011). Deep soil organic matter—a key but poorly understood component of terrestrial C cycle. *Plant Soil* **338,** 143–158.

Rumpel C., Chabbi A., & Marschner B. (2012) *Carbon Storage and Sequestration in Subsoil Horizons: Knowledge, Gaps and Potentials.* In: Recarbonization of the Biosphere. Lal R., Lorenz K., Hüttl R., Schneider B., von Braun J. (eds://doi.org/10.1007/978-94-007-4159-1_20

Saggar, S., Tate, K.R., Feltham, C.W., Childs, C,W., & Parshotam, A. (1994).Carbon turnover in a range of allophanic soils amended with 14C-labelled glucose,*Soil Biology and Biochemistry*. 26:9. Pgs. 1263-1271. ISSN 0038-0717.

Saidy, A. R., Smernik, R.J., Baldock, J.A., Kaiser, K., Sanderman, J., & Macdonald, L.M. (2012). Effects of clay mineralogy and hydrous iron oxides on labile organic carbon stabilisation, *Geoderma*, Vol. 173–174,Pgs. 104-110. ISSN 0016-7061.

Sánchez-García, C., Oliveira, B.R.F., Keizer, J.J., Doerr, S.H., & Urbanek, E. (2020). Water repellency reduces soil CO_2 efflux upon rewetting. *Sci. Total. Environ.*, 708 Article 135014.

Sanderman, J., Maddern, T. & Baldock, J. (2014). Similar composition but differential stability of mineral retained organic matter across four classes of clay minerals. *Biogeochemistry* **121,** 409–424.

Sanderman, J., Hengl, T., & Gregory J. Fiske, G.J. (2017). Soil carbon debt of human land use.*Proceedings of the National Academy of Sciences.* 114 (36) 9575 9580.

Scheidegger, A. M.; Sparks, D. L. A (1996). CRITICAL ASSESSMENT OF SORPTION-DESORPTION MECHANISMS AT THE SOIL MINERAL/WATER INTERFACE, *Soil Science*. Volume 161 - Issue 12 - p 813-831

Schlesinger, W.H., & Amundson, R. (2019). Managing for soil carbon sequestration: Let's get realistic. *Glob Change Biol*. 25: 386– 389.

Shi, Z., Allison, S.D., He, Y., Levine, P.A., Hoyt, A.M., Beem-Miller, J., Zhu, Q., Weider, W.R., Trumbore, S., & Randerson, J.T. (2020). The age distribution of global soil carbon inferred from radiocarbon measurements. *Nat. Geosci.* **13,** 555–559.

Schmidt, M. W. I., Torn, M. S., Abiven, S., Dittmar, T., Guggenberger, G., Dittmar, T., Guggenberger, G., Janssens, I.A., Kleber, M., Kogel-Knabner, I., Lehmann, J., Manning, D.C., Nannipieri, P., Rasse, D.P.(2011). Persistence of soil organic matter as an ecosystem property. *Nature* **478,** 49–56.

Sharma, A., & Hesterberg,D. (2020). 9 - Synchrotron radiation-based spatial methods in environmental biogeochemistry, Editor(s): Regina M.B.O. Duarte, Armando C. Duarte,

Multidimensional Analytical Techniques in Environmental Research. Elsevier. pgs. 231-265. ISBN 9780128188965,

Singer, M.J., & F.C. Ugolini. (1976). Hydrophobicity in the soils of Findley Lake, Washington. For. *Sci.*, 22. pp. 54-58.

Six, J., Elliot, E.T., & Paustian, K. (2000). Soil macroaggregate turnover and microaggregate formation: a mechanism for C sequestration under no-tillage agriculture. *Soil Biology and Biochemistry*. 32:14, 2099-2103. ISSN 0038-0717.

Six, H., Bossuyt, S., Degryze, K., & Denef. (2004). A history of research on the link between (micro)aggregates, soil biota, and soil organic matter dynamics. *Soil and Tillage Research*. 79:1. Pgs. 7-31. ISSN 0167-1987.

Steinbess, S., Beßler, H., Engels, C., Temperton, V.M., Buchmann, N., Roscher, C., Kreutziger, Y., Baade, J., Habekost, M. and Gleixner, G. (2008), Plant diversity positively affects short-term soil carbon storage in experimental grasslands. Global Change Biology, 14: 2937-2949.

Soil Carbon Center. (2012). *What is the Carbon Cycle?*. Kansas State University. Manhattan, Kansas.

Soil Survey Staff. Rapid Carbon Assessment (RaCA) project. United States Department of Agriculture, Natural Resources Conservation Service. Available online. June 1, 2013 (FY2013 official release).

Sollins, P., Swanston, C., Kleber, M., Filley, T., Kramer, M., Crow, S., Caldwell, B.A., Lajtha,K., & Bowden, R. (2006). Organic C and N stabilization in a forest soil: Evidence from sequential density fractionation. *Soil Biology and Biochemistry.* 38:11, 3313-3324. ISSN 0038-071.

Solly, E. F., Weber, V., Zimmermann, S., Walthert ,L., Hagedorn, F., & Schmidt, M. W. I. (2020). A Critical Evaluation of the Relationship Between the Effective Cation Exchange Capacity and Soil Organic Carbon Content in Swiss Forest Soils. *Frontiers in Forests and Global Change*. 3:98.

Sonan, L.S., Uttam, S. K, & Kissel, D.E. (2014). What are cation exchange and cation exchange capacity?. University of Georgia, Extension. Pg, 1-3.

Sumner, M. E., &Miller, W. P. (1996). *Cation Exchange Capacity and Exchange Coefficients.* pp. 1201-1229. 9780891188254.

Sun, S., Chevrier, D.M.,Zhang, P., Gebauer, D., & Cölfen, H., Angew.(2016). *Chem. Int. Ed. 55*, 12206.

Taghizadeh-Toosi, A., Olesen, J.E., Kristensen, K., Elsgaard, L., Østergaard, H.S., Lægdsmand, M., Greve, M.H. and Christensen, B.T. (2014). Changes in carbon stocks of Danish agricultural mineral soils between 1986 and 2009. *Eur J Soil Sci*, 65: 730-740

Tisdall, J.M. & Oades, J.M. (1982). Organic matter and water-stable aggregates in soils. *Journal of Soil Science,* 33: 141-163

Torn, M. S., Trumbore, S. E., Chadwick, O. A., Vitousek, P. M. & Hendricks, D. M. (1997). Mineral control of soil organic carbon storage and turnover. *Nature* **389**, 170–173.

Trumbore, S. (2009). Radiocarbon and soil carbon dynamics. *Annu Rev Earth Planet Sci* 37:47–66

Unger, S., Máguas, C.,Pereira, J.S., David, T.S., & Werner,C. (2010). The influence of precipitation pulses on soil respiration – Assessing the “Birch effect” by stable carbon isotopes. *Soil Biology and Biochemistry.* Vol. 42:10. Pgs. 1800-1810. ISSN 0038-0717, Vivies-Peris, V., de Ollas, C., Gomez-Cadenas, A., & Perez-Clemente, R.M. (2020). Root exudates: from plant to rhizosphere and beyond. *Plant Cell Rep* 39**,** 3–17.

Wan, M., Hu, W., Qu, M., Li, W., Zhang, JC., Kang, U.,Hong, Y., Chen,Y., & Huang, B. (2020). Rapid estimation of soil cation exchange capacity through sensor data fusion of portable XRF spectrometry and Vis-NIR spectroscopy. *Geoderma.* Volume 363: 114163. ISSN 0016-7061.

Wang, X., Cammeraat, E.L.H., Cerli, C., & Kalbitz, K. (2014). Soil aggregation and the stabilization of organic carbon as affected by erosion and deposition. *Soil Biology and Biochemistry*. Vol 72. Pgs. 55-65. ISSN 0038-0717,

Weber, J.W.J., Voice, T.C., Pirbazari ,M., Hunt, G.E., & Ulano, V.D.M. (1983). Sorption of hydrophobic compounds by sediments, soils and suspended solids – II. Sorbent evaluation studies. *Water Res* 17:1443–1452

Wershaw, R.L. (1986). A new model for humic materials and their interactions with hydrophobic organic chemicals in soil-water or sediment-water systems. *J Cont Hydr* 1:29–45

Wills S., Loecke T., Sequeira C., Teachman G., Grunwald S., West L.T. (2014). Overview of the U.S. Rapid Carbon Assessment Project: Sampling Design, Initial Summary and Uncertainty Estimates. In: *Soil Carbon*. Hartemink A., McSweeney K. (eds). Progress in Soil Science. Springer, Cham.

Wiesmeier, M., Urbanski, L., Hobley, E., Lang, B., von Lützow, M., Marin-Spiotta, E., van Wesemael, B., Rabot, E., Ließ, M., Garcia-Franco, N., Wollschläger, U., Vogel, H. J., & Kögel-Knabner, I. (2019). Soil organic carbon storage as a key function of soils - A review of drivers and indicators at various scales. In *Geoderma* (Vol. 333, pp. 149–162). Elsevier B.V

Yan, H., Yang, F., Gao, J. Peng, Z., & Chen, W. (2019). Subsoil microbial community responses to air exposure and legume growth depend on soil properties across different depths. *Sci Rep* **9,** 18536

Yusiharni, E., & Gilkes, R.J. (2012). Changes in the mineralogy and chemistry of a lateritic soil due to a bushfire at Wundowie, Darling Range, Western Australia. *Geoderma.* Vol. 191,Pgs. 140-150. ISSN 0016-7061.

Zaehle, S., Bondeau, A., Carter, T.R., Cramer, W., Erhard, M., Prentice, I.C., Reginister, I., Rounsevell, M.D.A., Sitch,S., Smith, B., Smith, P.C., & Sykes, M. (2007). Projected Changes in Terrestrial Carbon Storage in Europe under Climate and Land-use Change, 1990–2100. *Ecosystems* **10,** 380–401.

Zhang, X., Zhang, L., Zou, X., Han, F., Yan, Z., Li, Z.,& Hu, S. (2018). Semi-quantitative analysis of microbial production of oxalic acid by montmorillonite sorption and ATR-IR. Applied Clay Science. Vol. 162, Pgs. 518-523. ISSN 0169-1317,