

Final Report

The terrestrial carbon cycle and soils' role within a
Global Climate Change Mitigation Plan

By

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Abstract

The increase in greenhouse gas (GHG) emissions and the subsequent warming of the atmosphere are critical concerns for future climate conditions and their impacts on Earth's ecosystems. Among the GHGs, carbon dioxide (CO₂) accounts for a significant portion that continues to increase in concentration within the atmosphere, resulting in global temperature increases. According to the National Oceanic and Atmospheric Administration, 2015 was the warmest year on record, and in order to combat the harmful consequences of rising temperatures, there is an urgency to formulate policy and programs that reduce and sequester CO₂ emissions. One proposed approach is to promote carbon (C) sequestration in soils so that soils can function as a C sink by offsetting gaseous C emissions. The success of soil C sequestration depends on the precise quantification of soil C stocks, as well as the fluxes within them, and the use of informed site-specific management practices for different terrestrial ecosystems within Earth's system. This literature review focuses on the challenges in determining reliable estimations of soil C stocks, the capacity of soils to function as C sinks, and to review the proposed strategies, concerns, and critical needs in research for the implementation of soil C sequestration as a possible mechanism in stabilizing atmospheric CO₂.

Chapter 1. Introduction

There has been an increasing interest in soil science within the last few decades mainly driven by management of soil quality and fertility for crop production, as well as soil's potential

role in climate change mitigation. Soils are a viable component for helping to solve global climate change driven by increases in atmospheric CO₂ emissions.

A thorough assessment of the terrestrial C cycle and the soil C pool within is crucial to understanding soil's dynamic role in Earth's systems, and currently our understanding of the functionality of the soil system is still limited (Cao, 2015). Thus, before soil can be suggested to potentially function as a C sink, or as an offset of emissions, scientists must first accurately and precisely measure soil C pools, with reduced variability and assumptions, and which produce reliable results from study to study. The quantification of SOC stocks and changes within them as a result of the spatial and temporal variation at the continental scale need to be better understood (Cao, 2015). Once these methods have been established, then it is necessary to select the methods and approaches to be implemented for soil C sequestration based on the needs and function of a site-specific soil. The ability of soil to function as a means of C storage depends on the soil quality and capacity to store SOM. Thus, a prerequisite to a successful mitigation plan requires a full understanding of the many processes and interactions involved within the dynamic soil system. All methods of soil C sequestration must be considered, selected, and integrated into the overall plan based on a soil's capacity to function within the ecosystem in which it is located. Therefore, soil C sequestration must be viewed as a case by case, site specific and systematically determined approach prior its implementation into a global climate change mitigation plan. There is no single solution or method to be used, but rather a collaboration of methods in which soil can act as a global C sink. The following is a summary of strategies to address this issue.

1.2 Soils Role within the Terrestrial C Cycle

The geosphere, biosphere, atmosphere, and hydrosphere continuously cycle matter and transfer energy, collectively working together to balance Earth's system. At various rates, the terrestrial C pool plays an integral role in the global C cycle, pulling C from the atmosphere and releasing it again through decomposition. Atmospheric CO₂ enters the terrestrial pool through primary production, where it is stored in living tissue, and later subject to one of a few potential fates. Over time, the litter fall will accumulate, where it will decompose and be translocated by processes such as leaching, runoff, erosion, or stored in the soil C pool.

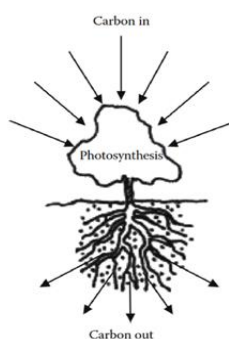


Figure 1.1. The action of plants as a C pump between atmosphere and soil (Geotherapy, 2015).

Soil is a major C pool within the global C cycle. The global soil C pool has been estimated at 2,500 Pg, with 1,550 Pg of SOC and 950 Pg of (SIC) (Batjes, 1996). Based on Stockmann et al., 2013, the soil C pool contains from 2000 to 2400 Gt of organic C in the top meter, not including the organic C in the cryosols, which has been estimated to contributing an additional 1300 Gt of C. It was also found that the above ground biomass accounts for about 600 Pg C (Wei-Dong, 2008), and together, the vegetation biomass and soil that is not affected by land use and land change, accounts for about 7% of the total SOC stocks (160 ± 90 Pg C) (IPCC, 2013). Furthermore, it was calculated that the amount of organic C within the global soil pool can be equated to being more than the amount of C that would be released for the next 200 years using the current amount of annual fossil C emissions (Stockmann et al., 2013). Therefore,

the significant role of soil in the global C cycle, climate change, and the Earth's system as a whole makes soil a valuable resource that must be thoroughly understood.

1.3 Soil Carbon Sequestration

Although the reduction in atmospheric CO₂ cannot be achieved solely by soil C sequestration, the soil C pool has great potential to alleviate the continued increase of CO₂ into the atmosphere. According to the Environmental Protection Agency, together the SOC sequestration from forest growth and agricultural offsets are about 13% of US fossil-fuel emissions (US EPA, 2008). When using the current best estimations of soil C stocks and rates, a rounded average of half a ton of C per hectare per year can be sequestered globally under best management cropping practices (McBratney et al., 2014). There is currently no certainty about soil's capacity to store C. However, the current knowledge of soil is substantial and can be used to make reliable predictions of soils ability to function as a C sink and to successfully offset C emissions.

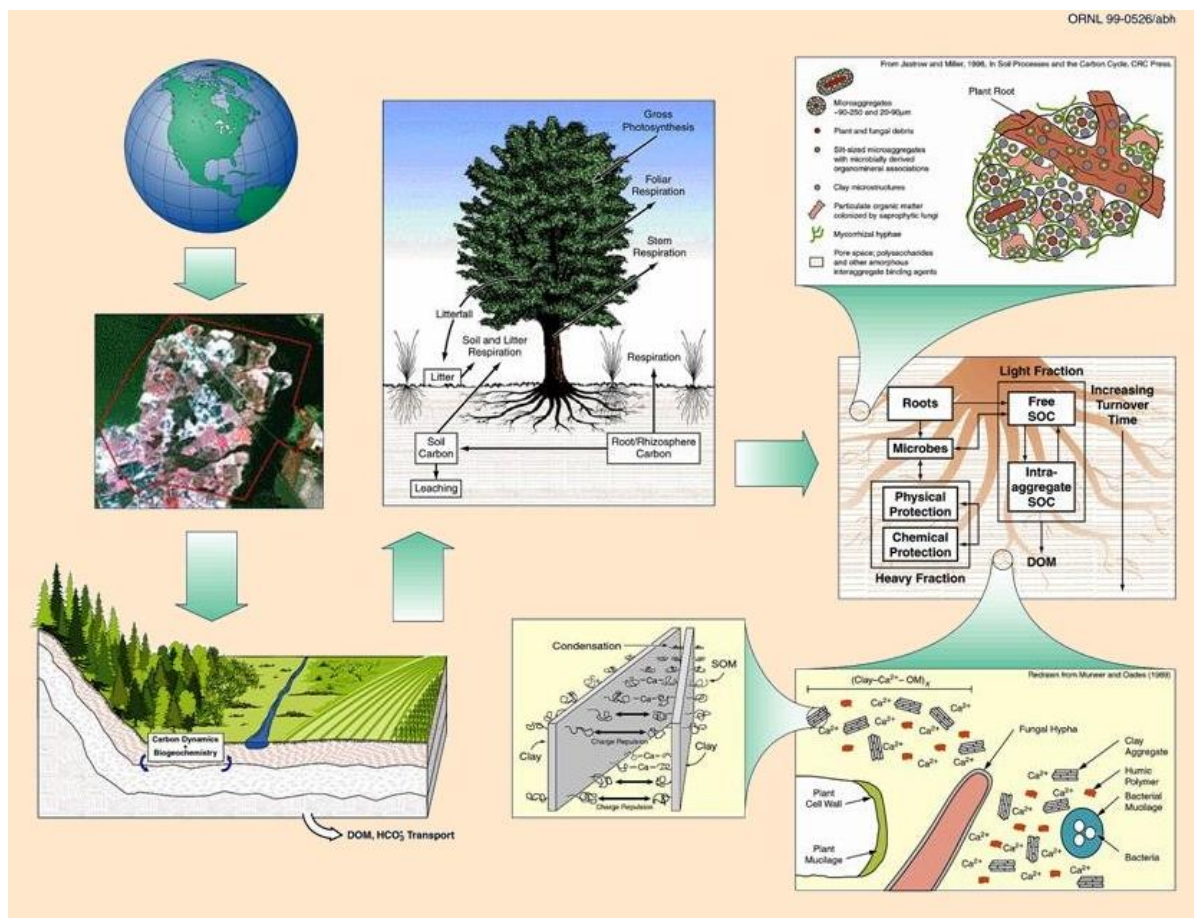


Figure 1.2. Investigating C sequestration processes across multiple scales, from CSiTE, ORNL.

A quality soil is a soil that has the ability to perform the functions necessary for its intended use, which is evaluated using inherent and dynamic soil properties. SOC has been identified as a key indicator of soil quality (McBratney et al., 2014). The critical concentration of SOC is the point at which soil's ability to function as a C sink is reduced significantly. It was found that the critical concentration level of a soil is 20 g SOC kg⁻¹ (2 % SOC) (McBratney et al., 2014), and the critical concentration level in the root zone is 1.5–2.0% by weight (Lal et al., 2015). Figure 1.3 displays the key properties involved in soil quality, with SOC required for all functions of a quality soil (McBratney et al., 2014).

On the opposite end of the spectrum, SOC saturation relates to the capacity at which soils can store C, which is limited due to the amount of fine particles in the soil (McBratney et al., 2014). Stockmann et al., 2013 produced a saturation curve of SOC accumulation as a function of the soil forming factors (soil texture, climate, soil material, time, and topography), identifying critical concentrations of SOC (McBratney et al., 2014). They found that the interactions of SOC with mineral surfaces and metal ions are the key factors in the stabilization of SOC (McBratney et al., 2014; Six et al. 2004), and that there was a limit to the soil's capacity to store or sequester C dependent on the processes involved in the interactions of soil mineral constituents and SOM (McBratney et al., 2014). However, soil properties serve as indicators of soil function, and it is important to note the observations may be subjective, thus making it very difficult to measure soil function directly (USDA, 2015). Therefore, having a full understanding of all of the factors that impact SOC turnover rates and accurate estimations of SOM is imperative for making reliable predictions on a soil's ability to offset C emissions by storing C.

Soil Quality Indicator	Soil Function				
	Sustain biological diversity, activity, and productivity "D"	Regulate and partition water and solute flow "W"	Filter, buffer, degrade, detoxify organic and inorganic materials "F"	Store and cycle nutrients and carbon "N"	Physical stability and support for plants and structures associated with human habitation "S"
Aggregate Stability ^{a,c,i}	★★	★★	—	★★	★★↓
Available Water Capacity ^{a,g}	★★★	★★↓	—	★★	—
Bulk Density ^{a,h}	★★↓	★★★	—	★	★★★
Earthworms ^{b,d}	★★★	—	★★★	★★★	★★★
Infiltration ^{b,e,i}	—	★★	★	—	—
Particulate Organic Matter ^{a,c}	★★★	★★★	★★★	★★★	★★★
Potentially Mineralizable Nitrogen ^{a,c}	★★★	—	—	★★★	—
Reactive Carbon ^a	★★	★	★★★	★★	★★
Slaking ^{b,e,i,j}	★	★★↓	—	—	—
Soil Crusts ^{b,d}	—	★★↓	—	—	—
Soil Electrical Conductivity ^b	—	★★★	—	—	—
Soil Enzymes ^a	★★★	—	—	★★★	—
Soil Nitrate ^b	★	★	—	—	—
Soil pH ^{b,d}	★★	★★★	★★★	★★★	—
Soil Respiration ^{a,b,c}	★★★	—	★	★★★	★★
Soil Structure and Macropores ^{b,d}	★★↓	★★↓	★	★	★★
Total Organic Carbon ^a	★★★	★★★	★★★	★★★	★★★

Figure 1.3. Soils function – indicator matrix, USDA (2015).

Chapter 2. Mechanisms controlling soil C turnover and their potential for enhancing C sequestration

Soil C sequestration capacity is the threshold of a soil's ability to retain and stabilize C. The accumulation does not solely depend on the quantity and quality of organic C additions, but also on the biochemical alteration and the physiochemical protection of SOC. Biochemical alteration coupled with the physiochemical protection of SOC is the basis of stabilization and accumulation. Biochemical alteration involves the transformation of SOC through biotic and abiotic soil forming processes to forms that are more chemically resistant to microbial decomposition, and in some cases, have a greater retention by sorption to soil solids (Jastrow, 2006). Therefore, the amount of time organic compounds persist in soils is directly related to intrinsic or developed resistance to further microbiological degradation (Torri et al., 2014). Then, depending on the soil texture and mineral constituents, physicochemical protection can stabilize SOC further reducing the turnover rate, which is the amount lost within a given period of time. Physicochemical protection, due to the organo-mineral interactions at molecular to millimeter scales, offers protection of SOC that ultimately inhibits biochemical attack (Jastrow, 2006). Therefore, increasing the residence time and reducing the rate of turnover through the physiochemical protection of SOC will eventually result in increased SOC.

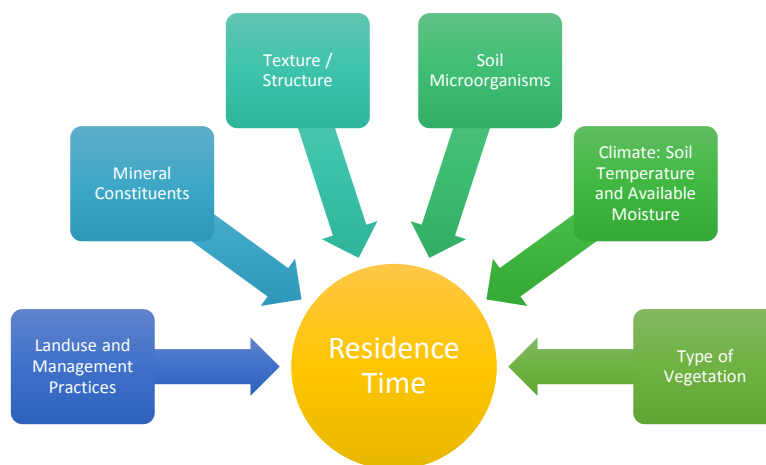


Figure 2.1. Residence time, Megan Hitchcock (2016).

The accumulation and stabilization of SOC require C inputs to exceed outputs. The average time that a SOM molecule resides in soil or the residence time, which is the amount of time from the point of entry into the soil C pool to the complete decay and loss as CO₂ (Bohn et al., 2015; Chen et al., 2013). Whereas the amount of C lost within a period of time is called the soil C turnover rate (Jastrow et al., 2007). The amount of time SOC is stored, or the residence time (τ), is a function of the capacity of the soil to store SOM (Jastrow et al. 2007; Luo et al. 2013). The increase in τ of SOM and the storing of SOC can be achieved even if there is not an increase in the inputs. However, this only holds true to a limit. The continued increase in soil C and the residence time are both dependent on the capacity of the soil to store C. Even if the residence time remains unchanged, the stabilization of soil C can only continue for as long as the mechanisms controlling τ remain unsaturated (Jastrow et al., 2007; Six et al. 2002), and soil biologic activity is the primary determinant in the decrease in residence time. The processes listed in Table 2.1 influence the susceptibility of SOM, thus impacting the residence time.

Table 2.1: Soil processes that influence susceptibility of SOM to degradation are:

1. Sorptive protection on minerals.
2. Occlusion in micropores.

3. *Specialization of decomposers towards different substrates.*
4. *Heterogeneous microhabitats in which different types of microorganisms are present.*
5. *Self-aggregation of organic molecules that protects parts of the molecules.*
6. *Adsorption of metals that makes the organic matter unavailable for degradation by microbes.*

Fires can also reduce the surface residence time, by generating charcoal beneficial in the stabilization of SOC, as well as enhance soil fertility (Amonette et al. 2009; Dai et al. 2005; Glaser et al. 2002; Jastrow et al. 2007; Post et al., 2004). Although natural events such as fire can reduce the residence times, biologic activity such as respiration and decomposition is the primary determinant in the decrease of SOC residence time. Environmental factors such as moisture, temperature, pH, or nutrient availability, which a function of the soil properties and soil forming factors of a given soil, control and can limit decomposer activity. Thus, restricting this activity or controlling the factors that promote the cycling of C back into the atmosphere would subsequently increase the residence time, stabilizing SOC, and ultimately contributing to soil C sequestration.

2.1a Biochemical Alteration and Physiochemical Protection

The biochemical alteration and physiochemical protection are the two mechanisms responsible for the stabilization of SOC and thereby control τ (Jastrow et al., 2007). Biochemical alteration is the chemical transformation of SOM by biotic and abiotic processes to forms that are more resistant to decomposition (Jastrow et al., 2007). The process of transforming of OM to a form that is somewhat resistant to further microbial attack is called humification. Soil organic matter or humus refers to the organic fraction of the soil exclusive of un-decayed plant and animal tissues, their partial decomposition products, and the soil biomass. The humus fraction or

SOC is the phase of C between photosynthetically fixed C and completely oxidized C to CO₂ (Bohn et al., 2015). The SOC fraction of the SOM represents 51% of the global terrestrial C, and to stabilize or increase this C pool, the mechanisms responsible for the stabilization need to be understood. However, it has been established that the resulting products of humification have varying degrees of microbial resistance and rates of turnover. And, although humus material takes more time than the labile pool to cycle out because it is somewhat resistant to further microbial decomposition, enhancement of the physiochemical protection of the humified material will significantly increase in the residence time of SOC (Jastrow et al., 2007).

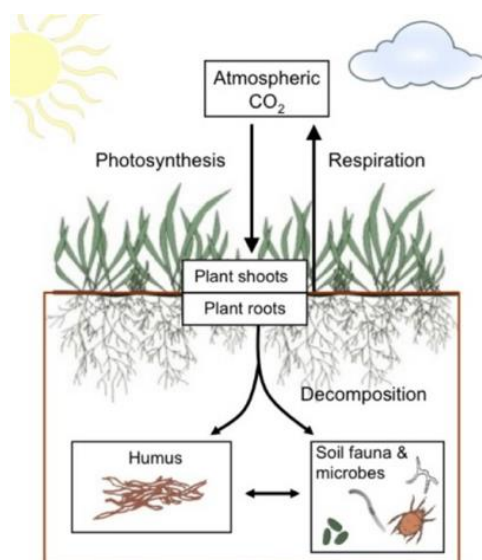


Figure 2.2. C balance within the soil (brown box) is controlled by C inputs from photosynthesis and C losses by respiration. Decomposition of roots and root products by soil fauna and microbes produces humus, a long-lived store of SOC. [Nature Education, 2012.](#)

Physiochemical protection occurs when organo-mineral interactions within a soil system inhibit biochemical attack of SOC (Jastrow et al., 2007). The physiochemical protection of SOM is achieved by processes such as sorption of SOM to the surfaces of solid soil constituents, complexation with soil minerals, occlusion within aggregates, and SOM deposition in pores that are inaccessible to decomposers and extracellular enzymes (Jastrow et al., 2007). Nevertheless,

although the biochemical alteration of SOM and physiochemical protection can stabilize SOC, both mechanisms are dependent on soil type, vegetation, microbial communities, as well as the environmental conditions present due to soil forming factors and management practices within a given soil (Jastrow et al., 2007).

2.1b Biochemical Alteration

The role of soil microorganisms and their association with specific soil processes are not entirely understood. For the most part, C stabilization involves the alteration of organic matter to forms that are more resistant to microbial attack, which can be further protected by absorption to soil solids, as well as other organo-mineral interactions (Jastrow et al., 2007). The consumed C and how efficiently microorganisms such as bacteria and fungi utilize the C have been reported to vary (Jastrow et al., 2007). Maximum decomposition occurs when sufficient nutrients, such as N, P, and other essential nutrients are available, yet not all decomposing organisms efficiently utilize the SOC. Low C utilization efficiency is when there is a greater amount of respiration of metabolized C as CO₂ (Jastrow et al., 2007). Thus, when metabolizing the same amount of C, organisms with lower utilization efficiency would result in a reduction in residence time and a decrease in storage as the rate of turnover is increased (Jastrow et al., 2007).

The differences between the organic compounds within microbial biomass is also an important factor in the fate of SOC. The cell walls in fungi contain complex molecules such as melanin and chitin which tend to persist in soils (Guggenberger et al. 1999; Holland and Coleman, 1987). Thus, fungal biomass formation and their nature of metabolism play an important role in C sequestration. On the other hand, bacterial membranes consisting predominantly of phospholipids, are rapidly metabolized by bacteria (Jastrow et al., 2006).

Another important factor involving soil microorganisms is the differing nature of the extracellular enzymes they produce (Jastrow et. al., 2006). Fungi produce large amounts of enzymes such as phenol oxidases, laccases, and peroxidases that contribute to the degradation of OM (Jastrow et. al., 2006). These fungi are saprotrophic in nature, meaning that they degrade complex organic compounds to acquire C. The monomers that are produced from degradation of lignitic materials are the principal constituents of humic materials, suggesting that an abundance of fungal enzymes should favor humification (Jastrow et. al., 2006). On the other hand, bacteria tend to produce lipases and cellulases, which are needed to attack nonlignitic materials.

While cellulose, a major component of plant cell walls, can readily be degraded by bacteria and fungi, a select group of fungi that produce the extracellular lignin and manganese peroxidases restrict the complete degradation of lignan (Conesa et al., 2002; Schubert, 1965; Teunissen, 2001). This 'selective degradation' allows for the labile portion of C to decompose first, progressively increasing the recalcitrant portion through time (Jastrow et. al., 2006). Decomposition of the recalcitrant C inputs can be achieved by these extracellular enzymes if not restricted by adsorption. Initially, these enzymes are subject to sorption by soil solids, however, once those adsorption sites are saturated, then enzyme activity within the soil can increase (Jastrow et. al., 2006). Enzyme production is then regulated by having to diffuse farther from the source to gather fewer materials for the microorganism that synthesized them, and by doing this, the cost exceeds the benefits for the organisms producing the enzymes (Jastrow et. al., 2006). However, in undisturbed soil, the hyphae can extend long distances for gathering nutrients, contributing in a network of bridges that increases the overall soil organic matter. In contrast, the limited mobility of bacteria in soil forces them to utilize substrates in close proximity. Because the biomass of bacteria is primarily comprised of the more labile energy-rich molecules such as

phospholipids and amino acids (Guggenberger et al., 1999), their remains tend not to accumulate or significantly contribute to SOC (West et al. 1987).

Mineralization is the biotransformation of organic matter into products such as CO_2 , NH_4^+ , and H_2O . Organic matter can be degraded aerobically in the presence of oxygen or anaerobically in an environment lacking oxygen depending on the soil environment, microbial communities present, and bioavailability of soil organic matter. Anaerobic microorganisms digest organic polymers such as the insoluble cellulose compounds during bacterial hydrolysis to soluble forms. The second stage of anaerobic digestion is called Acidogenesis, where acidogenic bacteria transform simple monomers such as sugars and amino acids into products such as organic acids, ammonia, and hydrogen ions. Then, during acetogenesis, organic acids are converted to acetic acid, hydrogen, or CO_2 releasing C back into the atmospheric pool. However, incomplete decomposition can lead to the formation of more resistant humus.

The formation of humus materials involves three main steps; partial decomposition of organic materials, synthesis, and polymerization. Extracellular enzymes primarily undergo the first stage of decomposition of insoluble organic compounds to more soluble forms.

Microorganisms then synthesize the soluble forms and converted to phenols and quinones, which are then further oxidized and undergo polymerization. When the monomers produced during synthesis, undergo polymerization, complex chains of polyphenols and polyquinones form by interacting with N-amino compounds to produce a more resistant form of humus. Thus, the presence of nitrogen can aid in the humification process.

The quality of humus formed depends on the soil depth, organic material, and soil texture, while the rate of humification depends on the plants, soil organisms, rate of decomposition, temperature, aeration, and moisture. Good aeration, near neutral pH and

sufficient soil moisture, tend to promote humification.

The C:N ratio also plays a role in the rate of decay. Residues of high C:N ratios force microorganism to compete for available N. OM containing high amounts of lignin and polyphenols decay slowly due to the high C:N ratio, making them the most recalcitrant organic components. Thus, the presence of polyphenol compounds can inhibit decomposition due to the presence of phenolics slowing oxidation and nitrogen fixations. Mineralization is slow initially with OM containing high lignin or polyphenols and a low C:N ratio, while OM containing low amounts of these compounds and low C:N ratio decay more rapidly initially. Most microbial organisms require a C:N ratio of 8:1, and if the C:N ratio is greater than 25:1, then microbes must scavenge the soil solution to obtain enough N, resulting in the depletion of N within the soil solution causing nitrate depression. Thus, the decay of OM can be delayed with insufficient N to support the microbial demands. Additionally, without continued additions of plant residues, microbial organism will oxidize humus and reduce the amount of SOM.

The three groups of humus include fulvic acid, humic acid and humin, all of which vary in solubility and turnover time. Fulvic acids are the most susceptible as they are soluble in both acid and alkali environments, reducing the turnover time (15-50yrs) when compared to humic and humin. Humic acids are soluble in alkali and have a turnover rate of greater than 100 years, while humin is insoluble in both alkali and alkaline, making them the most resistant to further microbial decay and increases the rate of turnover.

Mycorrhizal fungi can also be major contributors in the stabilization of SOC. Although, they are not directly involved in the decomposition of SOM, their symbiotic relationship with plants plays an important role in the stabilization of SOC. Mycorrhizal hyphae extend the roots of terrestrial plants, allowing a greater of volume of soil to be used as a nutrient source for plant

uptake, while the fungi benefit by obtaining photosynthate-C directly from the plant. Thus, mycorrhizal fungi contribute to sequestration as an additional C input to soil organic matter. However, even though mycorrhizal fungi can be a significant source of C inputs, having cell walls composed largely of chitin make them relatively resistant to decomposition (Zhu and Miller, 2003). Mycorrhizal fungi also produce a glycoprotein called glomalin that may be resistant to degradation and aid in aggregate formation (Steinberg and Rillig, 2003). In addition, mycorrhizal fungi contribute to the formation of soil aggregates, that aid in the stabilization of SOC (Miller and Jastrow, 1990; Tisdall, 1996; Tisdall and Oades, 1982). Together, mycorrhizal hyphae and plant roots help in stabilizing macroaggregates creating sticky-string bag that enmeshes and entangles soil particles (Miller and Jastrow, 2000; Oades and Waters, 1991).



Image 2.1. Mycorrhizae Hyphae proliferate within the mycorrhizae, which appears as off-white fuzz in this image. These hyphae greatly increase the surface area of the plant root, allowing it to reach areas that are not depleted of nutrients. Source: Boundless. Mycorrhizae: The Symbiotic Relationship between Fungi and Roots. Boundless Biology. Boundless, 08 Jan. 2016. Retrieved 18 Mar. 2016

2.1c *Physiochemical Protection*

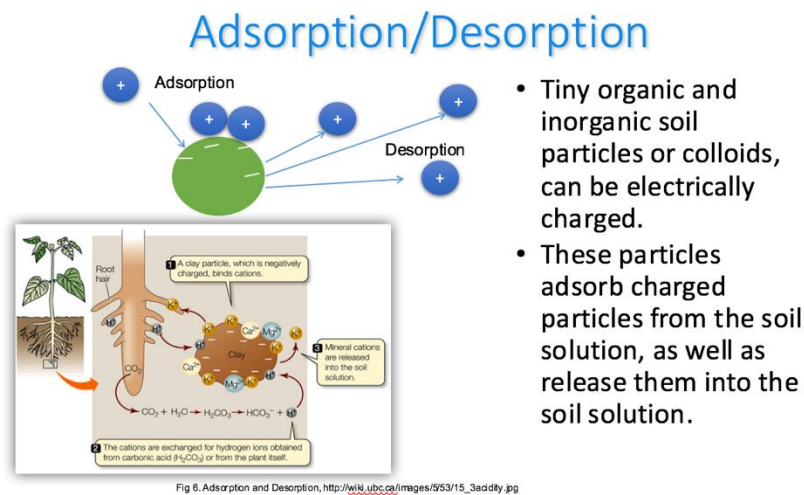
Physiochemical protection is achieved when SOM is protected from further microbial decomposition or oxidation by the presence of oxygen and extracellular enzymes, thus

significantly increasing the residence time of soil C (Jastrow et. al., 2006). The physiochemical protection of SOM can occur by either chemical and physical adsorption to soil solids, as well as the creation of barriers that protect against agents that would result in further decomposition or oxidation reactions.

Soil solids, particularly soil colloids, play a significant role in the physiochemical protection of the biochemically altered SOM. Soil colloids, particles ranging from 1 to 1000 nm in size, can reduce the impact of biochemical alteration, protecting SOC from further decomposition. Soil colloids consist of degraded plant material or humus and clay-sized mineral particles such as phyllosilicate clays, allophanes, and the oxides and hydroxides of Mn and Fe (Bohn et al., 2015). Although they are tiny in size, the large surface area of these charged particles provides a large interface to interact and exchange ions with the soil solution. This highly reactive fraction of soil is said to be a major focus of chemical and physical activity (Bohn et al., 2015). However, even though minerals with high specific surface area and adsorption capacities may provide the greatest protection, soils and their colloidal constituents vary, as do their surface area. Soils containing high amounts of smectite and vermiculite, such as alfisols and mollisols have a greater clay content, while highly weathered oxisols have reduced amounts of these soil colloids, thus low CEC. Therefore, physiochemical protection is greatly dictated by the type of soil colloids present.

The interface between soil solids and soil solution is known as the solid-solution interface. The large surface area of soil colloids provides a greater interface for increased reactions with the soil solution (Bohn et al., 2015). The solid-solution interface between the soil colloids and soil solution undergoes exchange reactions, removing particles by the process of adsorption, and then releasing ions by the process of desorption, both of which are controlled by

surface area and surface charge. Soil colloids with greater adsorption capacity have the ability to adsorb particles from the soil solution, making them unavailable, or otherwise protecting them from further microbial attack or decomposition. However, the charge and magnitude of charge on the surfaces of minerals changes as a function of pH. Similarly, organic matter has pH dependent charge, yet the net charge is usually negative. 2015).



- Tiny organic and inorganic soil particles or colloids, can be electrically charged.
- These particles adsorb charged particles from the soil solution, as well as release them into the soil solution.

Figure 2.3. Adsorption and desorption between soil solution and solids particles; Megan Hitchcock & Adsorption and Desorption, http://wiki.ubc.ca/images/5/53/15_3acidity.jpg

A commonly accepted mechanism for SOM stabilization includes the adsorption of SOM to the surfaces and interlayer surfaces of soil mineral particles (Kleber et al., 2007; Sollins et al., 1996; von Lützow et al., 2006). The sorption occurs via a variety of organo-mineral associations; polyvalent cation bridges, van der Waals forces, hydrogen bonding, and interactions with hydrous oxides and aluminosilicates (Jastrow et. al., 2006). The resulting stabilization is directly related to the amount of adsorption sites on the clay mineral surfaces. While there are many sorption and complexation interactions possible that can aid in the retention of SOM, the persistence of SOM depends on many other factors. Factors such as the reactivity and specific surface area of mineral components, base-cation present, the presence of Fe- and Al- oxides, pH,

and redox conditions within the soil environment (Baldock and Skjemstad , 2000; Blanco-Canqui and Lal, 2004; Oades 1984; Sollins et al., 1996).

The interactions of the solid-solution interface are dependent on the chemical characteristics of within the soil solution, such as ion charge, charge density, and radius of ions (Bohn et al., 2015). The ion charge, as well as the charge density of an ion, influence electrostatic interactions of ions with each other and soil particles (Bohn et al., 2015). Certain charged ions have a greater affinity for adsorption reactions, and when strongly adsorbed, they can be said to be removed from the active pool of the soil solution, and somewhat protected from microbial interactions.

Many soil mineral clay particles within the colloid fraction belong to the phyllosilicate group. Secondary phyllosilicates, or layered silicates, have large solid-solution interfaces that greatly influence soil properties. Some even have the ability to replace a structural ion, substituting it with an ion of similar size in a crystal lattice (Bohn et al., 2015).

1:1 phyllosilicates clays (kaolinite) consist of a single tetrahedral sheet joined to an octahedral sheet. These silicates clay do not allow isomorphic substitution and are generally considered electrically neutral because of the low the surface-charge densities (Bohn et al., 2015). These single layer silicates are non-expandable lacking an interlayer surface area for isomorphic substitution. The absence of the interlayer limits the exchange sites to the edges of the mineral surface; thus, there are fewer sites for SOM complexation. However, a study based on Brazilian Ferralsols reported by Dick et al. (2005) provided evidence that stabilization of organic matter is promoted mainly through surface interactions with iron oxides and kaolinite. Yet, Marques et al. (2011) suggested that there was a weak correlation between SOM and clay

contents in such soils (Velasco-Molina et al., 2014). Nevertheless, SOM may be sequestered and protected from microbial attack within such microaggregates.

In contrast, 2:1 phyllosilicates are sheet silicates with an octahedral sheet sandwiched by a tetrahedral sheet above and below. The space between layers, or the interlayer, contributes to the overall an overall increase in the specific surface area for potential exchange reactions with the soil solution. 2:1 phyllosilicates have the ability to undergo isomorphic substitution in either the octahedral or tetrahedral sheets (Bohn et al., 2015).

The interlayers of 2:1 secondary phyllosilicates are expandable, admitting water and exchangeable cations from the soil solution. Expansible 2:1 phyllosilicates greatly increase surface area, and the greater surface area and charge density result in an increase in cation exchange capacity. When ions of high charge density and ionic radius, are substituted into the crystal lattice the interlayer expands and the substitution leads to a negative surface charge. Thus, layers of 2:1 phyllosilicates commonly have permanent charge arising from this isomorphous substitution. The permanent net negative charge is then balanced by interlayer cations, and the 2:1 sheets bond electrostatically to charge-compensating cations in the interlayers. Interlayer cations balance a negative charge on the layer surface. The higher the charge per unit area, or charge density (e.g., cmol^+/m^2), the more cations in the interlayers, and the greater the interlayer charge, the more cations involved, resulting in a stronger the interlayer bond.

Upon substitution, the negatively charged silicate clays attract positively charged cations from the soil solution, forming a bridge for complexation with negatively charged organic groups (Bohn et al., 2015). Because of this substitution involved with 2:1 clay minerals, the availability of multivalent cations within the soil solution are an important factor in the chemical protection of SOC. Soils highly saturated with clays and multivalent cations acting as bridging agents can

then form organo-mineral complexes. As these complexes continue to increase, becoming more flocculated and condensed, there is a reduction in the efficiency of microbes and enzymes to further attack and decompose the SOC (Baldock and Skjemstad, 2000). Therefore, soil clay mineralogy and their specific surface area are important because they determine potential sites for interactions and provide potential protection of SOC (Baldock and Skjemstad, 2000; Kaiser and Guggenberger, 2003; Sollins et al., 1996).

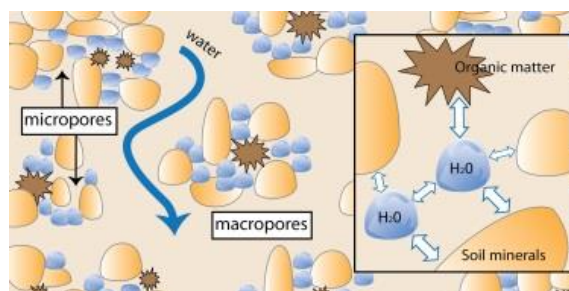


Figure 2.4. The make up of macropores, micropores, soil mineral, water and organic matter; <https://. qld.gov.au/environment/land/soil/soil-properties/water/>

Soil organic C can also be physically protected by physically impeding microbial access, or when the soil structure and connectivity of pores limits or reduces gas exchange and moisture conditions, thereby inhibiting decomposer activity (Elliot and Coleman, 1988; Elliot et al. 1980; Six et al., 2002a; Sollins et al., 1996; Young and Ritz, 2000). Therefore, the stabilization of SOC can be achieved through physicochemical processes that protect SOM by inhibiting the accessibility of microbes, oxygen, and moisture (McBratney et al., 2014).

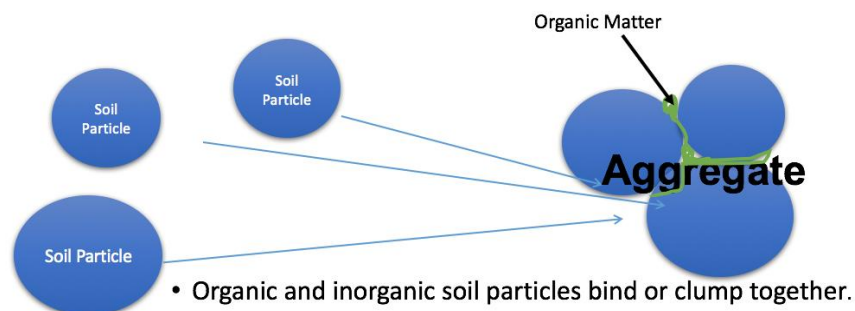


Figure 2.5. Formation of aggregates between minerals, and SOM, Megan Hitchcock.

The formation and stabilization of soil aggregates offers another means of physical protection of SOC from microbial decomposers. Soil particles of various size bind together and form larger masses called aggregate. Silt and clay size particles can bind together forming larger clumps called microaggregates. Then, microaggregates, along with silt-sized aggregates and primary particles, are bound the into larger macroaggregates (>250 μm diameter) by labile organic materials and by fine roots, fungal hyphae, bacteria, and algae. Thus, OM and its ability to act as a binding agent, aids in aggregate formation, increasing SOC stabilization, and reducing the rate of turnover (Dalal and Bridge, 1996; Feller and Beare 1997; Jastrow and Miller, 1998; Oades, 1993; Six et al., 2004, 2002b; Tisdall, 1996). The amount of long-term protection provided by macroaggregates may seem to be minimal; however, an increase in macroaggregate turnover can result in a decrease in SOC. Thus, these aggregates play an important role in the stabilization of SOC. In some cases, the turnover of macroaggregates may be required to incorporate and protect new C inputs from rapid mineralization. (Plante and McGill, 2002). Yet, if turnover is too rapid, then microaggregate formation and stabilization can be inhibited, reducing SOC protected by microaggregates, especially microaggregates that are occluded with particulate organic matter (Six et al., 2004).

The variation in aggregate size creates a parallel hierarchy of different pore sizes in and between the aggregates, controlling the gas exchange, water movement, and microbial distribution within the soil structure (Elliot and Coleman, 1988; Young and Ritz, 2000). The variation in texture and pore sizes can form physical barriers, providing physical protection of SOC. This can occur due to occlusion or encrustation of SOM with soil mineral constituents, as well as variation in the distribution in pore size and the tortuosity of pore (Bohn et al., 2015). The greater the tortuosity, the more difficult it is for microbial organism, gasses, and moisture to move through the soil. Therefore, pore size and connectivity controls microbial distribution and movement within the soil profile (Elliot and Coleman, 1988; Elliot et al. 1980; Young and Ritz, 2000), and together, flocculation, aggregation, and the subsequent occlusion can inhibit microbial accesses to SOC.

Bacteria, ranging in diameters of 0.2–70 μm , are the tiniest life forms. Because of this, most soil bacteria microorganisms cannot access labile C substrates within pores smaller than 1 μm or located inside larger pores with necks less than 1 μm (Bohn et al., 2015). Nano-scale pores can also offer similar protection from the diffusion of extracellular enzymes into micron-sized pores due to their relatively larger size (Zimmerman et al., 2004). Thus, clay mineralogy and size distributions play a fundamental role in reducing microbial and enzyme accessibility to SOC.

The soil structure and porosity can also reduce decomposer activity because of the limited movement of oxygen and water. The reduction of connected pores and subsequent decrease in gas diffusion can create steep declines in oxygen concentrations within small distances of the aggregates. Water can also interact with aggregate surfaces in and between pores creating water films, leading to patches of anaerobic conditions (Sexstone et al., 1985; Young and Ritz, 2000). It has been found that decreased decomposition can arise from the reduction in

organism motility, the diffusion of nutrients, toxins, and enzymes, and lower oxygen supply resulting from soils containing large volumes of pores with neck diameters $<4 \mu\text{m}$. These factors limit microbial habitats and reduce that ability of enzymes to access SOC due to the large distance, thereby preventing decomposition by the effect of the presence of an environment that reduces biological activity. Therefore, the microbial community and the many interactions involved coupled with the complexity of pore space and surfaces within their physical habitat can lead to SOC stabilization (Ekschmitt et al., 2005).

2.1d Physiochemical Protection and Podzolization as a means of C Sequestration

Podzolization is another proposed mechanism for accumulating SOC within certain soil environments containing iron (Fe) and aluminum (Al) bearing minerals. Podzolization results in a subsurface horizon with illuvial accumulation of active non-crystalline materials composed of OM and Al, with or without Fe, ultimately leading to subsurface C sequestration (Harris, 2015). Organic acids play a crucial role in the chemical weathering, metal mobilization, and then later complexation and flocculation of organo-mineral associations, leading to SOC accumulation.

The presence of organic acids can promote weathering of Al- and Fe-bearing minerals. The Al and Fe released via complexation with organic acids can remain in solution for a while, being protected by OM and mobile at the same time (Harris, 2015). When precipitation exceeds evapotranspiration, these organometal complexes can be transported downward within the soil profile; their depletion results in an eluvial (E) horizon. Over time, the organic acids can then form strong single or multiple bonds with Al and Fe resulting eventually in flocculation and

immobilization to form an illuvial horizon (Bh) enriched in inorganometal components (Harris, 2015).

Anderson et al. 1982 and DeConinck et al. 1980 proposed two mechanisms by which podzolization may occur. The Anderson explanation involves the separate vertical transport of amorphous metal silicates and DOC, eventually forming complexes at depth, resulting in accumulation of SOC in the lower horizons. The Anderson mechanism is based on the amorphous metals in the form of inorganic aluminosilicate colloids or dissolved species, which are released during weathering of minerals in the upper part of the soil. As negatively-charged organic solution species and colloids continue to be generated in the upper soil zone, they move downward and associate with the reactive, weakly crystalline, positively-charged aluminosilicates, resulting in accumulation due to increased Al- and Fe- concentrations (Harris, 2015). In contrast, DeConinck's explanation involves the release of metals from mineral weathering as promoted by organic acids, the joint vertical transport of associated metals and organic molecules or colloids, and ultimately the accumulation of these C- and metal-rich components in a subsurface horizon (e.g., Bh or Bhs) (Harris, 2015).

DeConinck's colloid theory, begins with DOC being released from litter decay, canopy drip, and root exudate. The DOC molecules have sites where H^+ can dissociate, behaving as acids. These acids can attack metals in minerals by forming strong bonds and breaking weaker mineral bonds, thereby promoting the weathering of these minerals. Lower pH would mean more protons chemisorbed to the organic colloids or molecules, reducing the negative charge and cloud size. The positive end of water molecules is attracted to the negative sites, making the DOC molecules hydrophylic (miscible in water), and capable of forming stable solution complexes with Al and Fe (Harris, 2015). That is, they form single or multiple bonds with the

ionic form of the metal which keep the metal in solution under conditions that it might otherwise precipitate and become immobile in the soil. The nature of the association between cation and molecule is dependent upon properties of the cation (radius, electron density, valence, etc.) (Harris, 2015). Valence is particularly important; the higher the valence, generally the stronger the cation-molecule association. Thus, Al^{3+} and Fe^{3+} are strongly bonded (chemisorbed) directly to the organic molecule or particle whereas Na^+ , K^+ and Ca^{2+} tend to form a loosely associated hydrated cloud around the particle via electrostatic attraction (Harris, 2015). A thick cloud promotes dispersion and mobilization because the positively-charged clouds repel each other. Hence dispersion and eluviation (E horizon formation) is favored by low valence of cations in the cloud (counterions) and high surface charge density of the particle (Harris, 2015). Continued chemisorption of Al^{3+} and Fe^{3+} as particles migrate downward in the soil reduces surface charge very effectively due to the high valence of these metal ions. This charge reduction in turn tends to reduce the thickness of the cloud. Flocculation and immobilization (illuviation; Bh horizon formation) of the originally mobile organo-metal complexes can occur when the cloud becomes thin enough that their force of repulsion is exceeded by mass-dependent attractive forces between particles (e.g., Van der Waals force) (Harris, 2015). Another possible flocculation mechanism is the linkage of particles to form larger particles by shared metal bonds (metal bridging) (Harris, 2015). Ionic strength is also a potential factor in flocculation because as it increases the cloud thickness decreases. Nevertheless, although this is a relatively new mechanism of the accumulation of SOC that is currently being researched, Podzolization can increase SOC, thus it must be integrated in the systematic solution in global C sequestration.

Chapter 3. Trends in Soil C Storage with Time

“Some people speculate about how much time is required to build an inch of soil material.”

The answer, “somewhere between 10 minutes and 10 million years”.

~ Charles Kellogg, Soil Survey Chief for the U.S. Bureau of Chemistry and Soils in the 1930's

3.1 *Soil C Turnover*

The quantification of C fractions and their various residence times or turnover times has recently been of interest in classifying various types of SOC (Conant, 2011). The average amount of time that SOM occupies the soil C pool until it is decayed and lost as CO₂ is called the C turnover time (Bohn et al., 2015). The C fluxes between these soil C pools are spatially dynamic, and shift as a function of changes in the land-use, climate change, and other environmental or human-induced stressors (Cao, 2015). And, the response of soil C dynamics from differences in these factors have a direct influence on both the future climate and the quality of ecosystems and the vital services these encompass (Mathieu et al., 2015). Soil fertility is also related to the dynamics of soil C (Tiessen et al., 1994). For example, excess N can result in soil acidification resulting in a loss of nutrients by the process of leaching.

Changes in SOC occur most readily in the SOM fraction (Donovan, 2013). The persistence of SOM varies due to temperature, water content, and the mineral composition of the soil, as well as a function of the organic C compounds in the soil (Bohn et al., 2015). The physicochemical and biological influences of the soil ecosystem that result in reduction SOM decomposition are key factors that determine the persistence of SOM (Schmidt et al. 2011). From complex biomolecules that slowly degrade, such as cellulose or lignin, to simple organic compounds that tend to degrade quickly, the persistence of SOC is ultimately an ecosystem property. Thus, given the importance of SOC for ecosystem processes and functions within the

biosphere, and its feedback into the atmospheric and influence on the rate of climate change, understanding the patterns and controls of SOC storage are critical (Jobbagy and Jackson, 2000; Raich and Potter, 1995, Trumbore et al., 1996, Woodwell et al., 1998).

3.2 *Climate and SOC turnover*

Among the soil forming factors, climate may have the most significant impact of the change of SOC (Cao, 2015). Climate plays a role in the physiochemical and biochemical preservation of SOC, and climate is a major determinant in the type of plant species, the amount of plant material produced, as well as the intensity microbial decomposition of SOM. Thus, global climate change may induce a change in the decomposition patterns of SOM by altering soil microbial communities and activities. In return, these shifts in the overall flux of C into and out of the soil may have a major impact on the soil fertility as well (Cao, 2015).

Although decomposition rates increase with an increase in temperature, this can be offset by CO₂-driven increases in NPP and soil inputs (Todd-Brown et al., 2014). However, there is still much uncertainty because there has yet been a long-term study on the response of heterotrophic respiration to changes in temperature and moisture (Cao, 2015; Jones et al., 2005).

As discussed in the section on podzolization, soils in tropical regions and interaction of organic matter with Fe and Al oxides and poorly crystalline minerals within these soil promote the stabilization of SOM protecting it from microbial decomposition, thus decreasing the rate of degradation (Bohn et al., 2015). Poorly drained soils also aid in preventing soil organisms from carrying out decomposition due to water inundation of plant debris and the subsequent reduced oxygen concentrations. In the absence of oxygen, fermentation can transform SOM, but the

decay of plant materials by fermentation is slow and insignificant in oxygen-limited environments (Bohn et al., 2015).

Climate can also impact the vertical distribution of SOC within a soil profile. Many studies have showed that temperature impact and interactions with moisture availability and vegetation type, simultaneously influencing the soil C production and decomposition throughout the soil profile (Fissore et al., 2009; Qi and Xu, 2001; Raich and Tufekciogul, 2000). In a study conducted by Cao et al., (2015), it was found that that the correlation between temperature and precipitation variables are stronger in 0-20 cm profile than they are in 0-100 cm profile. In their study, they found that 30-year average maximum temperature in August negatively correlates with SOC stock (Cao, 2015). In another study based on the Inner Mongolian grasslands of China, it was found that there was a significant negative correlation with mean annual temperature and a significant positive correlation between SOC and the average annual precipitation in the 0-20 cm and 20-40 cm layers (Cao, 2015; He et al., 2014) Therefore, mean annual temperature may have a greater impact on SOC that precipitation, with the temperature sensitivities of decomposition outweighing the impact of lack available water for plant and microbial activity within the soil system (Cao, 2015).

The physical heterogeneity of a soil and the microclimates within them affect the rate of decay, as does the climate of a given region. Microbial decomposition will proceed as long as there is an adequate amount oxygen, water, temperature, and nutrient available for the decomposing organisms. Soil aggregates and structure can result in a variation in microclimates within a soil profile. Within microenvironments, lacking oxygen and water, there is a reduced rate of decomposition. Whereas, the rate of decomposition may be faster deeper in the soil profile, in locations that have the required water available for microbial decay. Therefore, both

microclimates or regional climates, impact the rate of decay. Understanding this relationship between turnover rate and climate conditions is imperative to finding the capacity of a soil to store.

3.3 Soil texture and SOC turnover

Fine soil texture and the reactions these particles undergo have a significant influence on the physiochemical protection of SOM, thus resulting in a reduced rate of soil C turnover. It has been well established that the SOM content tends to increase with an increase in soil clay content. The interactions of the mineral constituents and the SOM can physically isolate the SOM protecting it from microbial decomposition, or inhibiting degradation. One important mechanism is the aggregation and occlusion of soil organic matter between colloids, and the tiny pores within the profile that limit diffusion O₂ needed for degradation. As discussed in the previous section on physiochemical protection and podzolization, the presence of metals (i.e. Al³⁺) that complex to the organic functional groups can limit SOM degradation. Also, the highly reactive 2:1 clays and their high adsorptive capacities for organic molecules, can aid in protecting nitrogenous constituents of SOM from attack by microorganisms (Bohn et al., 2015). Therefore, soil texture plays a major role in SOC turnover rate.

3.4 Types of Vegetation, Net Primary Production and Rate of SOC turnover

Plant litter and roots are the primary sources of SOC inputs. Thus, the net primary production (NPP) and the produced litter fall within a certain region are requisites for accumulation and stabilization of SOC. The annual input rate of plant litter varies widely among ecosystem types. The type of plants that thrive within certain ecosystem can significantly affect

the overall vertical distribution of SOC (Jobbagy and Jackson, 2000). In humid tropical forests, litter input rates are large, and in deserts litter input rates are minimal. Root debris and root exudates are an important source of soil C in the lower profile. In forest soils, plant roots are responsible for up to about half of the total plant-derived C input to soils, and about one-third in grasslands (Jobbagy and Jackson, 2000). Additionally, Shi et al., 2013 reported that in forest ecosystems, it was the plant communities that had a major influence on the soil fungal communities through their role in the provisioning of carbon. Nevertheless, for a given soil and ecosystem, a steady-state SOM can be achieved. However, the steady state can shift depending on the natural processes or management processes that change the vegetation and soil conditions. And, given the dynamics of this system, it can be challenging in finding the balance between the NNP and the rate of decay based on vegetation and climate, yet understanding these relationships and the many processes involved is necessary to make predictions of a soils capacity to store C as climate continues to change.

3.5 Soil Type, Climate, and the Vertical Soil Profile C Dynamics

Until recently, it was thought that together climate, vegetation, and soil microbial communities had the greatest control on the soil C pool. However, in 2015, Mathieu et al., reported on the influence of soil type and its role in the dynamics of deep soil carbon. It was suggested by Mathieu et al., 2015, that radiocarbon activity (D14C) may improve the overall understanding of the rates of soil C biodegradation and stabilization. In their study, a four parameter model was used to produce predictions of soil D14C with depth, soil type, climate, vegetation, and land-use (Mathieu et al., 2015). They found that the C in topsoil was primarily affected by climate and cultivation, while soil taxa had a great effect on the sub soil than by

climate. It was the amount and activity of clay minerals that had contributed to the stabilization of C within the deep soil, illustrating the strong dependence of the pedologic traits and mineralogy on soil C dynamics (Mathieu et al., 2015). Table 3.1 presents the deep soil C activity, soil type, and deep soil mineral phase (Mathieu et al., 2015). According to the table, andosols have a very high reactive clay content, nanominerals of the allophane type, aiding in stabilizing large amounts of organic matter. A greater amount of stabilization was also found in soils containing high-activity smectite clays in combination with exchangeable Ca saturation, specifically the vertisol and chernozem groups (Mathieu et al., 2015), supporting the role of surface sorption in the physiochemical protection of organic matter from microbial biodegradation. Mathieu et al., 2016 concluded that soil pedological type and specifically dry climates were the primary drivers affecting deep soil carbon; Figure 3.1 Cwa. Similarly, a study conducted by Cao et al., 2015 found that the SOC stocks are mainly governed by the parent material, climate, ecological interactions, and environmental covariates, and to lesser extent by biotic and topographic variables (Cao, 2015). They also concluded that the main drivers in the change of SOC are climate and land use type, as well as socio-economic factors (Cao, 2015).

3.6 Soil Organisms and SOC Stabilization

The net decomposition of SOC must be equal to, or less than, the C inputs for the stabilization of SOC, soil microbes play an important role in the process of biochemical alteration of SOM into a more resistant form called humus. It has been established that 1g of soil can have 10^6 – 10^8 bacteria cells and several km of fungal hyphae (Bohn et al., 2015). Soil microbes significantly contribute in the mineralization of organic carbon, mineralizing 80–95% of plant matter and 50% of SOM is derived from microbial biomass. Furthermore, not only do

soil microbes aid in the transformation of SOM to more resistant forms, but some soil microbes such as symbiotic fungi can lead to 70 percent more C stored in the soil (Averill et al., 2014).

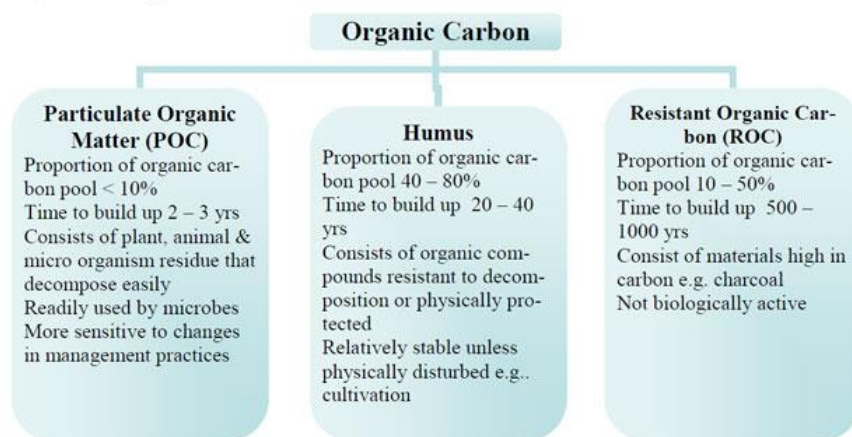


Figure 3.1. Soil Organic C Pool, *Sue Briggs, DEPI Rutherglen*, <http://agriculture.vic.gov.au/agriculture/dairy/news-events-and-webinars/dairy-newsletters/mountain-milkline/may-2013/soil-carbon-on-dairy-farms>

The organic material additions will break down through microbial, enzymatic, and chemical reactions. The rate at which organic C inputs decay is a function of the soil texture, mineral constituents, climate, and properties of organic material, as well as the type of microbes and the extracellular enzymes in which they produce within the soil system. For example, the soil texture and mineralogy can inhibit degradation by adsorbing SOC, making it unavailable to soil microbes, thus reducing rate of decay. Occlusions can also inhibit decomposition by limiting microbial access to SOC. The physiochemical protection of SOC reduces the C available for microorganisms, leaving behind the non-degraded material and microbial cells. These materials will then bind, forming aggregates, assembling through hydrophobic and molecular forces with ions and minerals forming humus. And, the final stage of litter decomposition is the gradual loss of the more resistant plant compounds, amongst which lignin is the most prevalent.

3.7 Fungal Communities, Vegetation, and SOC Accumulation

A recent study investigated the variation in fungal communities within forests in China with a change in latitude. They collected samples from 17 forests in China including boreal, temperate, subtropical and tropical forests (Shi et al., 2013), then correlated their data with abiotic and biotic variables within each forest to identify the factors that had the strongest influence on fungal community composition (Shi et al., 2013). They reported that temperature, latitude, and plant diversity had the strongest influence on the soil fungal community composition (Shi et al., 2013). They concluded that in forest ecosystems, it was the plant communities and their role in provisioning of C that had the greatest control on the soil fungal communities (Shi et al., 2013), and that the fungal diversity was highest in forest systems with the lowest tree diversity. Additionally, the dominant fungal communities differed within each forest. Boreal and temperate forests were dominated by ectomycorrhizal fungi, while tropical rainforests had a greater population of endomycorrhizal fungi, and in the subtropical forests, it was the non-mycorrhizal fungi that were best represented (Shi et al., 2013). And based on their results, it was suggested that soil fungal communities have a strong dependence on the type of vegetation and that there was an inverse relationship between plant and fungal diversity, with a high level of fungal speciation occurring in less diverse forest systems (Shi et al., 2013). This is important because fungi and their symbiotic relationship with vegetation significantly contribute to SOC stabilization.

3.7 Mycorrhizal fungi and SOC Stabilization

Most plant species on the Earth rely on a symbiotic relationship with mycorrhizal fungi to acquire nutrients from soil, and the role of these fungi is currently unaccounted for in global climate models (Averill et al., 2014), and can lead to 70 percent more C stored in the soil. EMM

Fungi, (ecto- and ericoid mycorrhizal) release a variety of enzymes for acquiring N from SOM, and in some cases, compete with other decomposing microbes in the process (Averill et al., 2014), thus reducing the amount of decomposition, as well as the amount of CO₂ released back into the atmosphere. Whereas, AM or arbuscular mycorrhizal fungi do not produce these enzymes. It was found that ecosystems dominated by EEM fungi store 1.7 times more C per unit of soil N than ecosystems dominated by AM fungi (Averill et al., 2014) because the enzymes produced allow EEM fungi to extract more N from the soil than the AM fungi. Thus, the presence of these fungi are critical for plant function and even more for stabilizing SOC. This study also found that mycorrhizal status has a greater effect on soil C content than the NPP, clay content, and climate variables. One reason is that EEM fungi and other free-living microbes are in competition in for organic N within the soil. Because of the variation in mycorrhizal functional traits, their control on decomposition and soil C storage can be just as significant as the chemical and physical properties of soil that tend to protect OM. Thus, the identity and functional traits of soil microorganisms play a fundamental role in controlling terrestrial C cycle. And, until recently there has been little demonstration or appreciation of the different types of symbiotic fungi that colonize plant roots and their control on the global C cycle. Therefore, global changes that result in the alteration of soil environments and the competitive interactions for N between decomposers will in turn affect soil C storage at regional to global scales (Averill et al., 2014). And the intimate relationship between vegetation and mycorrhizal fungi must be considered developing models to produce accurate predictions about the future C cycling.

The lack of research on the balance between the temporal and spatial dynamics in the soil C pool makes it a great challenge to quantify and make predictions of the changes within the SOC pool. Although there is much knowledge on the properties that contribute to the

biochemical alteration and physiochemical protection of SOC, as well as the many relationships within the dynamic soil system, the many different methods that are used globally for soil sampling and chemical analyses, coupled with the simplified models, produce much uncertainty for making SOC estimations. In a study reported in 2015 based on C turnover times which used a state-of-the-art coupled climate C-cycle models concluded that there remains a wide variation between models that may underestimate the global τ rate of turnover as much as by 36% (Carvalhais et al., 2015). This latitudinal pattern shows that there is a temperature dependency, identifying the increase in residence time with an increase in latitude, which is consistent previous research on the temperature controls on ecosystem dynamics (Carvalhais et al. 2015). Therefore, more accurate predictions and estimations of SOC require the improvement of methods for acquiring data and the models produced. (Bohn et al., 2015). Precise predictions in size of the vegetative, atmospheric, and soil C reservoirs, and the rate at which C moves between them are necessary for modeling C fluxes. There is a need for the development of integrated models using soil properties, soil forming factors, management practices, and the interactions involved in the ecosystem services that soil provides, as well as potential changes that may develop in response to the current shift in climate.

Chapter 4. Soil Carbon Stocks

4.1 Determining Soil C Stocks

Quantifying C sources, sinks, and ecosystem processes that modulate the global C system is critical to identify imbalances and counteract global climate change. What and how you measure SOC depends on the intended goal of the study and what the results are going to be used for (Donovan, 2013).



**Table 3: Default reference SOC stocks (SOC_{REF}) for mineral soils³
($tC\ ha^{-1}$ in 0-30 cm depth)**

Climate region	HAC soils ^(a)	LAC soils ^(b)	Sandy soils ^(c)	Spodic soils ^(d)	Volcanic soils ^(e)
Boreal	68	NA	10	117	20
Cold temperate, dry	50	33	34	NA	20
Cold temperate, moist	95	85	71	115	130
Warm temperate, dry	38	24	19	NA	70
Warm temperate,	88	63	34	NA	80
Tropical, dry	38	35	31	NA	50
Tropical, moist	65	47	39	NA	70
Tropical, wet	44	60	66	NA	130
Tropical montane	88	63	34	NA	80

^(a) Soils with high activity clay (HAC) minerals are lightly to moderately weathered soils, which are dominated by 2:1 silicate clay minerals (in the World Reference Base for Soil Resources (WRB) classification these include Leptosols, Vertisols, Kastanozems, Chernozems, Phaeozems, Luvisols, Alisols, Albeluvisols, Solonetz, Calcisols, Gypsisols, Umbrisols, Cambisols, Regosols; in USDA classification includes Mollisols, Vertisols, high-base status Alfisols, Aridisols, Inceptisols);

^(b) Soils with low activity clay (LAC) minerals are highly weathered soils, dominated by 1:1 clay minerals and amorphous iron and aluminium oxides (in WRB classification includes Acrisols, Lixisols, Nitisols, Ferralsols, Durisols; in USDA classification includes Ultisols, Oxisols, acidic Alfisols);

^(c) Includes all soils (regardless of taxonomic classification) having > 70% sand and < 8% clay, based on standard textural analyses (in WRB classification includes Arenosols; in USDA classification includes Psamments);

^(d) Soils exhibiting strong podzolization (in WRB classification includes Podzols; in USDA classification Spodosols);

^(e) Soils derived from volcanic ash with allophanic mineralogy (in WRB classification Andosols; in USDA classification Andisols)

Figure 4.1. SOC Stocks for Mineral Coils, UNFCCC (2013).

Assessment of the terrestrial C cycle and the soil C pool within is crucial to understanding soil's dynamic role in Earth's system. Before soil can even be suggested to potentially function as a C sink, or an offset of emissions, scientists must first determine an approach using methods that accurately and precisely measure soil C pools, with reduced variability and assumptions, producing reliable results from study to study. Although, precise methods for determining soil C pool have been established, spatial variability within the SOC pool and the many factors that induce changes, make it difficult to document change (Conant et

al., 2011). Therefore, it is importance to include historic soil data in digital soil models to aid in predicting actual SOC stocks. In addition, spatial resolutions of soil C data for most parts of the world are in various ranges, so that soil C estimations are divergent in different regions (Sanchez et al., 2009). This is because the quantification of changes in SOC stocks relies on a set of measurements that are extrapolated in various ways to represent a larger geographic area (Conant et al., 2011). Therefore, accurate and cost effective soil organic C stock estimations are imperative when considering SOC as a C sink in order to achieve desirable emission reduction targets prior to integration into a Global Climate Change Mitigation plan.

Plot soil samples can be collected and used to determine soil C content within a localized area, yet on a regional, biome, or global scale, estimations of the size of C reservoir becomes less accurate due to assumptions involved in modeling, lack of soil properties, and the dynamic processes involved in ecosystem services (Bohn et al., 2015). Based on the current literature, the estimates of the total global SOC reservoir ranges from 1500 to 3500 Pg C (Bohn et al., 2015). Global estimations of SOM differ due to depth of soil sampling used for calculations, errors involved in the extrapolation of soil C data across a given landscape, and the scarceness of measurements for a region. Therefore, more accurate predictions and estimations require the improvement of methods in acquiring data and the models produced. Precise predictions in size of the vegetative, atmospheric, and soil C reservoirs, and the rate at which C moves between them are necessary for modeling C fluxes. Although, it has been suggested that increasing the number of measurement sites will also likely reduce uncertainty in SOC stocks (Ogle et al., 2010), there is still a need for the development of integrated models using soil properties, soil forming factors, managements practices, as well as the interactions involved within the

ecosystem services that soil provides. Future models must include the many ecosystem processes that affect C fixation and loss to have a full understanding of soils role in climate mitigation.

4.2 *Methods in Determining Soil C Stocks*

The soil pool contains more C than the atmosphere and forests combined (Donovan, 2013). The organic matter in soil is a massive C sink within the terrestrial C reservoir with SOC representing 51% of the global terrestrial C. Soil organic C (SOC) is the difference between total soil C (TSC) and the inorganic C fraction (SIC), and when measured separately, the SOC content can be determined (Chatterjee et al., 2009). This C pool is mainly composed of soluble organic compounds, amorphous organic compounds (humic acid, fat, waxes, lignins and polyuronides), and organomineral complexes (Schnitzer, 1991) while the inorganic soil C pool includes primary and secondary carbonates (Eswaran et al., 1995). Unfortunately, this massive reservoir of soil C cannot be accurately measured directly in the field; therefore, soil samples must be collected and processed in the lab for the determination of SOC.

It has been established that the methods for determining soil C with high precision is an essential requisite for successful soil C sequestration (Chatterjee et al., 2009). Methods need to be developed that detect rate of change of soil C through specific time periods in order to quantify site-specific benefits. Whether it is the cost, variation in results, or production of harmful byproducts, all of current in-situ and ex-situ methods used in determining SOC have drawbacks associated with them.

Based on the current literature, possible mechanisms for determining soil C include; dry combustion or elemental analysis, wet combustion, acid treatments, C fractions, soil respiration,

bulk density (Conant et al., 2011). In-situ methods include remote sensing and spectroscopic measurements such as near infrared and mid-infrared.

4.3 *Ex-situ methods for Estimating Soil C Stocks*

Ex-situ methods in determining soil C stocks involve the collection of representative soil samples and measuring the C concentration using either dry or wet combustion techniques (Chatterjee et al., 2009). Both the wet and dry combustion techniques involve the oxidation of organic matter with an acid treatment, then measurement of the produced CO₂ by gravimetric, titrimetric, or manometric methods. The acid treatments are used to distinguish organic and inorganic C, in soils containing carbonates or other inorganic C constituents (Conant et al., 2011). Thus, to measure the organic and inorganic C separately requires acidification, as well as two dry combustion tests (Conant et al., 2011), reducing the efficiency and increasing cost.

4.3a *Wet combustion*

Wet combustion, introduced by Schollenberger in 1927, is regarded as a standard procedure in analysis SOC content. The wet combustion methods presented in the literature vary based on the type and concentration of the acids used and whether external heat is applied or not (Chatterjee et al., 2009). In this method, SOM is oxidized to CO₂ using a solution containing potassium dichromate, sulfuric acid, and phosphoric acid. When heated to 210°C, the carbonaceous material can be sufficiently oxidized. Then, the excess Cr₂O₇ was not used in oxidation is titrated with Fe (NH₄)₂ (SO₄)₂ 6H₂O, and the reduced Cr₂O₇ is then assumed to be equivalent to the soil organic matter of the sample (Chatterjee et al., 2009). However, it is assumed that the C present in soil has an average valence of zero.

Wet combustion has been modified over the years, including the type of acid used, the concentration, and whether or not an external heat source is used. Schollenberger (1927) suggested heating the soil mixture to complete SOM oxidation, thereby increasing the recovery; however, the heating temperature and duration may result in loss of SOC (Chatterjee et al., 2009). It was later determined that a standard temperature and length of heating must be established to ensure complete oxidation of a constant proportion of SOM (Chatterjee et al., 2009). The Walkley-Black method is one method of wet chemistry which uses a potassium dichromate solution ($K_2Cr_2O_7$) without external heat to determine SOC. This titrimetric method in determining CO_2 produces variable SOC recovery, as well as the generation of hazardous byproducts such as Cr, that can pose environmental problems associated with disposal (Chatterjee et al., 2009). To account for the incomplete digestion involved in this non-heating method, Walkley and Black (1934) suggested using a factor of 1.32 (assuming 76% recovery). However, this factor is dependent on soil type, soil depth, and mineralogy, which may not be applicable due to the heterogeneity of soils (Chatterjee et al., 2009). The WB was later modified by Tinsley and Mebius in order to enhance recovery by using an external heat source. However, the recovery is variable depending on the properties of the carbonized materials, resulting in overestimation of the SOC content, while the WB method (no external heat) results in underestimations of the SOC percentage recovered containing carbonized materials (Chatterjee et al., 2009; Heans, 1984; Skjemstad and Taylor, 1999; and De Vos et al., 2007). Low SOC recovery in wet digestion may also result from the presence of a high percentage of recalcitrant SOM, or by the presence of carbonized materials (e.g., charcoal, coal, coke and soot) (Chatterjee et al., 2009). Therefore, although this method is widely used, it has many drawbacks that need to be improved for the production of accurate estimations.

The titrimetric wet combustion is not only less precise, resulting in poor recovery, but requires careful analytical techniques, and may not fully account for the presence of charcoal or other types of organic matter (Conant, 2011). For example, in highly reduced soils, interferences by chloride (Cl⁻), ferrous iron (Fe²⁺), higher oxides of manganese (Mn³⁺ and Mn⁴⁺) and coal particles entail incorrect estimations of SOC content (Nelson and Sommers, 1996) as they are oxidized resulting in positive or negative error. Thus, a primary cause of variability in the percent of SOC recovered using the WB method is a function of soil type, textural class, and pedogenic horizons (Chatterjee et al., 2009).

Increased precision of wet combustion has been achieved by either using colorimetric analyses in place of titrations (Soon and Abboud, 1991), or using automatic titration or digital burettes, along with the wet digestion process (Chatterjee et al., 2009). An alternative method is using the Van-Slyke-Neil apparatus, a manometric determination of CO₂, which is less expensive, but involves an apparatus that can be easily damaged (Chatterjee et al., 2009). Ray Weil and others have discovered a method that may give an earlier indication of soil C change, by measuring the active C in soil using potassium permanganate wet chemistry (Conant, 2011). Nevertheless, despite the limitations due to the variations in percent recovered, wet combustion is used worldwide to measure SOC concentration due to the low cost and minimum requirements involved in this method (Chatterjee et al., 2009).

4.3b Dry combustion

Another ex-situ method is dry combustion. This process involves the incineration of SOM, thermally decomposing carbonate minerals, and then measuring the generated CO₂ (Chatterjee et al., 2009). The dry combustion test oxidizes and measures total soil C: organic

matter, charcoal, and carbonates (Conant, 2011). The two methods of dry combustion are as follows: dry combustion followed by measuring the changes in mass by loss-on-ignition (LOI), and, (2) dry oxidation of SOC, then collecting and determining the evolved CO₂ with automated instruments (Chatterjee et al., 2009).

4.3c *Loss on Ignition*

Rather (1917) introduced the technique of estimating SOM from the weight loss of soils on ignition (LOI). In this method, SOM is determined by putting the samples of the carbonaceous compounds in a muffle furnace at high-temperature ignition and measuring the weight loss from a dry soil sample (Chatterjee et al., 2009). The dry combustion, weight-loss-on-ignition, determines CO₂ gravimetrically; however, this method tends to result in an overestimation of SOM. When using this approach, it has been found that there was a substantial loss of the SOM due to temperature and duration of heating (Schulte et al., 1991). LOI can decompose inorganic constituents, producing CO₂, without igniting the entire SOM pool; therefore, it does not represent the whole SOC pool. This method also may have interferences with water, which minimize percent recovered. Some minerals containing molecular water; such as the structural water from clay minerals, amorphous materials (volcanic soils), and hydrated salts, release water at higher temperatures. So, drying the sample at low heat (105C) can lead to incomplete dehydration, resulting in an overestimation in SOC recovery values, soils containing low SOM and high clay content. Mitchell (1932) recommended a low-temperature ignition method to remove the water, while Jackson (1958), suggested using an induction furnace, which generates heat from high-frequency electromagnetic radiation (Chatterjee et al., 2009). However, it has been found that there is a substantial effect on the loss of SOM due to temperature and

duration of heating (Schulte et al., 1991). Even when using Rather's suggested method of first destroying the hydrosilicates by treating the samples with hydrochloric and hydrofluoric acids to eliminate the loss of hydroxyl groups during heating (Chatterjee et al., 2009), it was still found that SOM is prone to decompose during this treatment. Therefore, there is great difficulty in predicting an optimum temperature and duration of ignition ensures optimal SOM recovery while avoiding loss of SOM from the dehydration of clays (Chatterjee et al., 2009).

Not only can temperature, duration, soil texture and type affect the SOC recovery, soil sample size can also be a source of variation in LOI measurements (Konen et al., 2002). The sample size used must be large enough to detect changes and generate representative data within the limits of its combustibility. However, this is contradictory to what Schulte et al. (1991) reported, stating that the LOI values significantly decreased as the size of the sample increased and that this approach is difficult to carry out with samples larger than a few grams. The decrease in LOI values with increase in sample size was due to incomplete conversion and the generation of large amounts of gas to be measured (Pallasser et al., 2013). When using this method, it is also assumed that LOI values are a result of the combustion of solely the SOM and that the C content of SOM is constant (Christensen and Malmros, 1982). The use of an autoanalyzer or by the multiplication factor of 0.58 can be used to determine the SOC, yet this is assuming that SOM comprises 58% of the SOC. However, the conversion factor (0.58) used for extrapolation varies with the soil's type, depth of sampling, and types of organic compounds in the SOC (Chatterjee et al., 2009). Nevertheless, this method is simple, rapid, and an inexpensive technique of determining SOC content, yet the LOI-SOC regression equation must be identified for each soil type and depth for recovery of SOM, as well as the determination of the proper sample size, temperature, and duration of heating (Chatterjee et al., 2009).

4.3d Automated C Analyzer

Tabatabai and Bremner (1970) introduced a method of using an automated CO₂ analyzer based on thermal conductivity and the measurement of the effluent gasses (Chatterjee et al., 2009). It is the most accurate laboratory test for SOC and SIC, and this widely accepted method is currently considered as the standard method to determine soil C concentration. This form of dry combustion uses an elemental analyzer such as those made by Leco, Perkins-Elmer, Elementar, or Carlo Erba (Conant, 2011), yet it should be noted that this method of CO₂ detection varies with instruments, manufacturers, and models used. The automated dry combustion, using thermal conductivity, gravimetric, and IR absorption spectrometry, are all rapid, simple and precise. However, it must be noted that this method is very expensive and when carrying out this method, there is a slow release of contaminant CO₂ from inorganic carbonates with the resistance furnace (Conant, 2011; Chatterjee et al., 2009).

This method involves three phases: (i) Automatic introduction of the sample into a high-temperature oxidation zone wherein soil C is converted to CO₂ ; (ii) carriage of CO₂ by a carrier gas (generally He) and separated from other gasses (N₂, NOX, H₂O vapor, SO₂) either by a gas chromatographic system, or a series of selective traps for the individual gasses; and, (iii) detection of the concentration of CO₂ mainly by thermal conductivity, mass spectrometry or infrared gas analyzing methods (Smith and Tabatabai, 2004).

As do all of the methods mentioned so far, this method has its limitations. It has been found that precision is generally better when the samples are finely ground (< 177 μ m) (Chatterjee et al., 2009). Soil samples that are extremely small in size with low SOC content

generated very low detector signal-to-noise ratio, resulting in poor accuracy and precision (Chatterjee et al., 2009; Jimnez and Ladha, 1993). However, many studies found that approximately 100 mg of soil sample is adequate to obtain the best results (Chatterjee et al., 2009). Just as the LOI and wet combustions methods, incomplete combustion can result from differences in temperature and duration of heating. It was observed that under lower combustion conditions (1040°C) the carbonate decomposition from samples of pure CaCO₃ is minimized to 5%, whereas at higher temperatures (1300°C) it is maximized to 98%. The auto analyzer can be a valuable tool in measure SOC because it is rapid and precise, there is no loss of soil C during combustion, it can measure N and S, and it can be connected to a mass spectrometer for stable isotope analysis (Chatterjee et al., 2009). However, this method is more expensive due to the high cost of purchasing the analyzer and associated components (US \$40,000 to over \$50,000), and unless there is intensive soil sampling, the detection of changes in soil C over large landscapes due to spatial heterogeneity is very difficult (Chatterjee et al., 2009; Freibauer et al., 2004).

When comparing the different ex-situ methods for determining SOC stocks, the automated dry combustion analysis provides the highest precision when compared to wet combustion and dry combustion. The modified wet combustion Walkley-Black method tends to over-estimate SOC when soil samples contain extremely low SOC. Additionally, even though the WB procedure is considered to be cheap and relatively easy to perform, it may exhibit variable recovery; thus, this method requires a correction factor to determine the total SOC content for a soil sample. Although, the LOI method is advantageous due to the low cost (Chatterjee et al., 2009), neither dry combustion methods measure the total C or the inorganic C content (Chatterjee et al., 2009). LOI is however widely used to determine SOM and SOC, but

there is no standard temperature or duration of heating to be applied for the heterogeneity of soils. Additionally, the non SOC loss from heating can significantly effect the results of SOC.

4.3e Other Ex-Situ methods: soil respiration and bulk density

Soil respiration can also be used to measure soil organic C by measuring the CO₂ emitted by microbial respiration, acting as an indicator of microbial biomass; however, there is uncertainty in the direct correlation of microbial decomposition and the soil organic matter or total C (Conant, 2011).

The bulk density of a soil sample can be used to measure soil C based on the fact that OM is lighter than most mineral matter, so if organic matter increases in soil, the density will likely decrease (Conant, 2011). Bulk density, dry weight (g) of the soil sample, divided by the volume (cm³), is measured by oven-drying the sample to remove moisture, and weighing it. However, the heterogeneity of soils results in spatial variation, introducing error when extrapolating large regions (Conant, 2011). In a study conducted by Cao et al. (2015), developed a pedo-transfer function for bulk density (BD), to account for are missing values of BD in datasets, (Cao, 2015). BD predictions can be made for a given volume of intact soil, and the field-moist BD measurement currently provides the closest approximation to the actual mass of soil at the time of sampling (Cao, 2015).

4.4 In-Situ Methods in Estimating Soil C Stocks

In situ methods are non-destructive means of estimating soil C stocks with increased accuracy, and reduced time and cost when compared to conventional field soil sampling and laboratory analyzes (Chatterjee et al., 2009). These methods offer high precision with reduced

processing time and subsequent analysis (Chatterjee et al., 2009). The current in-situ methods include infra-red Reflectance, near-infra-red (NIR), mid-infra-red, laser-induced breakdown spectroscopy (LIBS), and inelastic neutron scattering (INS). Examples of these techniques include; the mounting of a near infrared probe on an implement pulled through the soil (Christy, 2008), or the use of gamma-ray spectroscopy from inelastic neutron scattering. The gamma-ray spectroscopy may enable field-wide measurements of SOC stocks (Wielopolski et al. 2008), through observation of SOC-stock covariates (Simbahan et al., 2006; Conant, 2011). Although these methods can reduce the time and provide reliable results, they require calibration with soil sampling and subsequent analysis using the automated dry combustion method; therefore, this application is limited due to the high cost of acquiring such data and the need for laboratory calibration (Pallasser et al., 2013).

4.4a Infrared Reflectance Spectroscopy

Infrared Reflectance Spectroscopy offers a simple, rapid, and low-cost measurement of soil C, measuring the organic and inorganic C pools simultaneously. This technique is based on measuring the reflectance radiation of illuminated soil (Chatterjee et al., 2009; McCarty et al., 2002). This approach involves the measurement and analysis of the NIR and MID inference reflectance values for the quantification of soil C (Moron and Cozzolino, 2002; McCarty et al., 2002; Russell, 2003). The NIR region consists of the 400–2500 nm range, and the MID is from 2500–25000 nm. NIR range is used to quantify the components of complex organic compounds, which is based on the absorption of the C-H, N-H, and O-H groups found in organic compounds, whereas the MID spectroscopy involves the spectral interpretation of chemical structures (Chatterjee et al., 2009).

The main disadvantage of using the MID and NIR reflectance spectroscopy is that the results may lead to spectral distortions and nonlinearities due to the strength of absorptions. Soil moisture content results in surface smearing effects, reducing accuracy. And, differences in particle size and soil mineral absorption intensities, can cause nonlinearities related to the individual soil matrix components (Russell, 2003). Because of this, it difficult when quantifying soil due to heterogeneous particle size and variable moisture content. The distribution of particle size affects the degree of scattering (Stendberg et al., 2010). For example, coarser textures result in increased scattering with lower reflectance; thus, NIR requires a need for continual calibration and quality control (Stendberg et al., 2010). However, when applied to a calibration set of samples of a similar particle size distribution, NIR offers excellent performance, simultaneously measuring certain quantitative and qualitative soil parameters, including types of soil C (Chatterjee et al., 2009).

4.4b LIB Laser-induced breakdown spectroscopy (LIBS)

This rapid method analyzes the unique spectral signature of C with the use of a laser beam set at a particular wavelength (Stendberg et al., 2010). The laser is focused on each sample using a 50mm focal length forming a microplasma that emits light characteristic of the sample's elemental composition (Ebinger et al., 2006; Stendberg et al., 2010). The emitted light is spectrally resolved using a grating-intensified photodiode array detector and intact soil cores or pressed samples are then analyzed, and the spectra collected along a soil core or from each discrete sample (Stendberg et al., 2010). This method is also capable of remote surface chemical analysis and measuring N, P and K, giving an indication of soil fertility, quality, and soil health (Chatterjee et al., 2009). This high precision method of determining SOC provides data at 1 mm

resolution; however, roots and rock fragments may cause variability in the C signal. Also, the sample size has to be quite large when compared to other methods (Chatterjee et al., 2009). Just as with NIR Reflectance Spectroscopy, soil properties such as texture, carbonate and moisture content can affect results. Thus, numerous calibration curves based on soil texture are required. Nevertheless, this rapid and portability method in determining SOC has great potential to collect and analyze thousands of measurements to characterize soil C content, its distribution and heterogeneity over a large area, yet future research is needed to reduce the variability in the LIBS signal caused by the presence of rock fragments and roots (Chatterjee et al., 2009).

4.4c Inelastic neutron scattering (INS)

Inelastic neutron scattering (INS) is a Nondestructive, multi-elemental, scanning modality with an analytic response function. This method of analyzing soil C is based on spectroscopy of gamma rays resulting from fast neutrons interacting with the nuclei of the elements in soil (Chatterjee et al., 2009). The INS unit is mounted on a cart, positioned to hover about 30 cm above the ground for an interval between 30 to 60 min. Using a neutron generator, neutrons penetrate the soil and stimulate gamma rays that subsequently are detected by an array of detectors (Chatterjee et al., 2009). The INS subsequently analyzes the acquired spectra for spectral peak intensities (counts) and, using an established calibration line, reports the results as kg C m^{-2} (Wielopolski et al., 2008). The soil's elemental content is proportional to (C, Si, O, N, H, Al, and K) the peak areas measured spectra (Chatterjee et al., 2009). The main advantage of this rapid scanning method is that it is insensitive to chemical configuration, capable of measuring multiple elements. Another advantage, given that soils tend to vary spatial, is that small variations in the soil bulk density have negligible effect on the interrogated volume.

However, regardless of vertical differences in BD, The INS system is directly calibrated in g C cm^{-2} representing the total C in the column below a unit area (Chatterjee et al., 2009). Once the system is calibrated, the exact amount of C measured is determined by conventional methods of sampling and dry combustion analysis. The presence of large or coarse fragments reduce the amount of soil/volume, thus reducing the C signals. INS being a nuclear method is insensitive to chemical configuration of the C. However, by measuring additional elements; such as Ca and Mg, it might be possible to partition SIC and SOC. The initial cost of the system is estimated at about \$150,000, yet there are no additional consumable costs are involved and the radioactive sources are shielded preventing any environmental hazards (Chatterjee et al., 2009).

4.4d Remote Sensing

Remote Sensing is another nondestructive method for SOC estimations. This method measures the reflectance values of various spectral bands that have been correlated with soil properties (Chen et al., 2000; 2007). This method involves the use of developed spectral sensors to measure SOM (Pitts et al., 1983; Griffis, 1985; Smith et al., 1987; Shonk et al., 1991). The sensors used usually operate with wavelengths between $0.3 \mu\text{m}$ and 1m , that are then divided into the following four groups: visible ($0.4\text{--}0.7 \mu\text{m}$), reflective infrared ($0.7\text{--}3 \mu\text{m}$), thermal infrared ($8\text{--}14 \mu\text{m}$), and microwave ($1 \text{mm}\text{--}1\text{m}$). It has been found that a wavelength between $0.4 \mu\text{m}$ to $2.5 \mu\text{m}$ is suitable for soil with $> 2\%$ SOM content (Baumgardner et al., 1970). Research shows that there is a linear relationship in the light reflectance of the visual and infrared range making it possible to predict SOM content (Baumgardner et al., 1970; Henderson et al., 1992; Smith et al., 1987; Sudduth and Hummel, 1988).

Through many studies it has been proven that accurate mapping of SOC can be achieved with remote sensing; however separate sampling and mapping for each location is required. Also, even though a strong relationship exists between spectral data and SOC content, predictions at different spatial scales has not to be accomplished. Moreover, to draw reliable inferences of SOC content from satellite imagery at large scales there is a need to develop indices such as vegetation type and species or soil moisture (Merry and Levine, 1995). Nevertheless, remote sensing offers high-resolution monitoring that is applicable for predicting SOC distribution. All methods discussed have pros and cons, and the method of choice should be selected based on specific measurement needs and applications. Therefore, the selection of an instrument or measurement techniques used ultimately depend on the researchers' needs and available resources, such as the project objective and allotted funds for the project.

4.5 *Challenges in Determining Soil Organic C Stocks*

Although there are various methods in estimating SOC stocks, there are also many challenges that need to be addressed.

Challenges include:

- Reliable methods in the removal of Inorganic carbon
- Variability in SOC stock due to sample depth, method used, and representation of data.
- Detection of changes due to alterations in land use and management practices
- Presence on quantification of coal and charcoal within soil
- Unified representation of data
- Thorough assessment of the terrestrial C cycle and the soil C pool within it providing accurate and precise estimations.

4.5a *Reliable methods in the removal of Inorganic C*

Reliable methods for the removal of Inorganic C needs to be established. Incomplete dehydration, the temperature required, and heating time can all impact the results. With the current ex-situ methods, there is great difficulty in predicting an optimal temperature and duration of ignition to maximum the recovery of SOM. The prime temperature and duration must be determined to avoid C loss by the dehydration of clays or decomposition of other soil constituents (Chatterjee et al., 2009). Additionally, LOI can decompose inorganic constituents, producing CO₂, without igniting the entire SOM pool; therefore, it does not represent the whole SOC pool.

4.5b Depth of soil sampling and spatial variability

The depth of soil sampling and the spatial variability within the soil profile can also impact estimations. The amount of C within a soil can vary depending on the soil texture, landscape position, drainage, plant productivity, and soil density, making it difficult to quantify any changes in the SOC stocks with time (Chatterjee et al., 2009). Also, spatial variability of soil C pools due to the many complex ecosystem processes within the soil system dependent on many environmental factors such as C inputs, substrate quality, temperature, water, microbial communities, and stressors, making the quantification of SOC stocks and flux a major challenge (Cao, 2015). The chemical and physical processes of soil formation are the driving factors for the spatial pattern of SIC within a given soil profile, whereas the biotic processes are they key controls for the spatial patterns of SOC within a given soil profile (Shi et al., 2012). Therefore, the variability of soil C with depth (>30 cm) needs to be better represented. Models to estimate SOC must include the many processes and dynamics involved within a soil system representing the whole soil profile (McBratney et al., 2015). Although there have been many studies reporting

the dynamics of the surface layers of soil C, the subsoil C remains poorly understood and quantified (Trumbore & Czimczik, 2008; Rumpel & Kogel-Knabner, 2011; Harper & Tibbett, 2013). The current procedures used produce unreliable estimations of the total SOC pool, partly because the available knowledge based on previous studies have not clearly defined upper soil horizons, nor have they included the significant contribution of subsoil to SOC stocks. Therefore, the soil expert community needs to work together in creating standard protocols of soil surveying and lab procedures in order to produce reliable local, regional, and global SOC pool estimates. The use of long-term ecological research sites that have monitored and quantified the changes in SOC changes and the underlying mechanisms are investigated, need to be the foundation for a unified approach for a regional, national, and international SOC monitoring programs (Jandl et al., 2013). The development of Mechanistic SOC simulation will play a vital role in future SOC monitoring programs as they can improve the estimation of temporal trends in the SOC pool; however, the current models are not yet adequate for the extrapolation of existing soil information over space and time (Jandl et al., 2013).

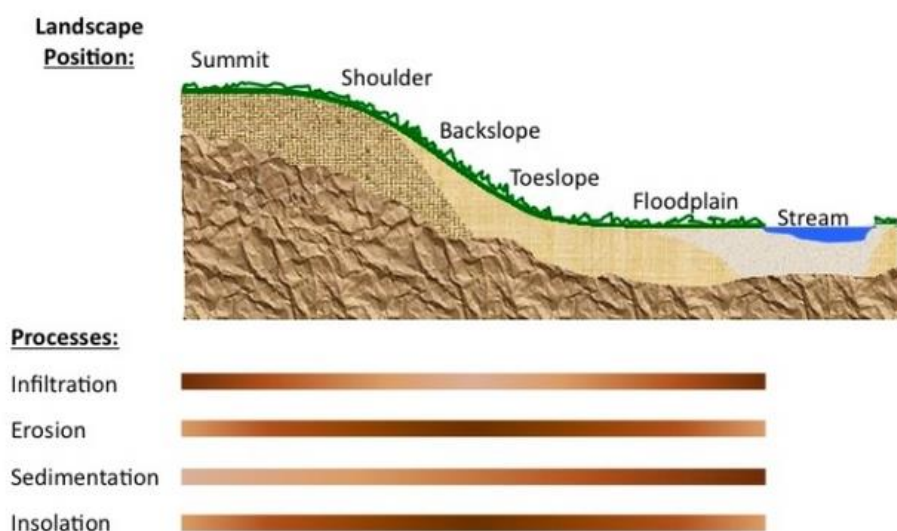


Figure 4.2. Landscape heterogeneity due to landscape position along a hill slope and possible effects on biophysical processes that effect C inputs and losses. Darker areas on bars indicate higher rates. Photo courtesy of Todd Ontl (2012), Nature Education.

4.5c Detection of changes within the SOC stocks

Detection of changes in the SOC stock due to alterations in land use and management practices is currently a major challenge when estimating SOC stocks. Based on the literature reviewed, the current methods in place do not adequately identify small changes over time in response to alterations in land use or land change, or soil management practices (Chatterjee et al., 2009). Soil C turnover rates can vary due to management practices, available moisture, and changes in local and global temperatures, and there is a need to identify methods for determining the rate of change in the soil's C pool over a specific period of time. Also, a standard protocol for evaluating the SOC pool and flux over multiple scales that includes the quantity of the site-specific additional benefits of soil C sequestration needs to be established (McBratney et al., 2014). To make sound decisions in a soils ability and capacity to store C, the detection and quantification of changes in the ecosystem dynamics of C is required (Chatterjee et al., 2009). Additionally, there is still much uncertainty of the terrestrial C emissions from land use change because the current rates of deforestation or the biomass density of tropical forests not well known (Houghton et al., 2009). Furthermore, it has been found that the subsoil contains C that was unaccounted for in previous models. Therefore, there is a need for future research and development in the production of models that signify changes in SOC stocks in relation to management practices for the soil profile to a depth of 1 m (McBratney et al., 2015).

4.5d Precise and accurate quantification of coal and charcoal with SOC stocks

The presence and quantification of coal and charcoal within soil can produce unreliable results. There are several established methods using thermal or chemical oxidation to quantify

charcoal C; however, the percent recovered varies widely. This is because charcoal is a mixture comprised of a wide range of particles, from large fragments of slightly charred biomass (1–100 μm) to submicron soot particles (30–40 nm) (Hedges et al., 2000; Masiello, 2004; Hammes et al., 2007; Chatterjee et al., 2009). Nevertheless, coal-derived C can be quantitatively measured by radiocarbon (^{14}C) activity. However, this method is expensive, results vary, and the facilities required for analysis are limited.

4.5e Representation of data

Representation of data is another challenge in SOC stock estimations. The units used for representing data are not always consistent from study to study. SOC is usually stated as grams C per kilogram soil, while the C pool is often denoted as area (Mg/ha), or even as volume (Mg/m^3) (Chatterjee et al., 2009). Quantifying SOC in terms of area also requires bulk density, depth increments for soil sampling, rock and root fragments, all of which vary spatially depending on the soil. For example; Soil bulk density varies due to gravel content, organic matter, and shrink-swell soils. Because the spatial variation and its significant influence in calculating bulk density, SOC estimations are not entirely precise, producing uncertainty in the measurements.

4.5f Lack of sharing up-to-date and relevant soil data

Another challenge is the lack of sharing up-to-date and relevant soil data and research within the scientific community. This is mainly due to the fact that the soil classification system and methods used for collecting and quantifying SOC stocks are inconsistent. Also, soil C stocks are in constant flux, resulting in out of date data sets, and there is a need for continued and ongoing monitoring of the soils system to produce reliable and current estimations of SOC stocks

and the changes within them. Additionally, the present scientific knowledge on the relationship between SOC and environmental covariates that cause changes in SOC stocks is not well understood (Hengl et al., 2014). Furthermore, most of the data is based on simplified models factoring in few environmental covariates; thus, future models need to be based on the integration soil forming factors and environmental covariates that exist within a soil system.

Despite the fact that there is a large amount of soil data in information that can be used to make prediction and decisions for future policy on soil's role in climate change mitigation, many of the current studies available differ in the techniques used in determining soil C measurements, sampling densities, sample protocols, environmental covariates, and statistical and geostatistical methods used to predict soil properties (Cao, 2015).

Chapter 5. The vertical distribution of SOC and its relation to climate and vegetation

5.1 Soil C variation within a soil profile due to climate, vegetation and soil type

The soil C pool is measured as the difference between inputs (NPP) and outputs (ultimately, microbial decay); however, the C distribution can vary with depth over a period of time due to differences given climate, parent material, topographic location, vegetation type, as well as management practices and land use and land change. According to authors Jobbagy and Jackson (2000), in the article based on the vertical distribution of soil, the SOC pool contains approximately 2344 Pg C when measured to a depth of 300 cm. However, Hiederer and Kochy (2011) estimated approximately 2469 Gt C (1Pg = 1Gt) measuring from 0-200cm, while Lal et al., (2004) reported that the soil C pool may contain as much as 2500 Gt C. Despite the fact that these estimations vary, the central point of this discussion is that the amount of C within a given

soil profile varies with depth, due to differences in climate, vegetation, and soil type, with soil type having the greatest influence on the deep soil C dynamics (Mathieu et al., 2015), while climate and vegetation having a greater control on the amount of C within the surface of a soil (Mathieu et al., 2015). Soil C stabilization in deep soil layers can also be a function of the ecological or trophic limitations of OM biodegradation (Fontaine et al., 2007), a direct result of soil mineralogy, texture and structure (Mathieu et al., 2015).

Humid climates have higher NPP than arid regions, however; the rate of decomposition increases with temperature. In dry regions, NPP is limited due to annual precipitation, yet decomposition is constrained, resulting in a greater amount of soil organic C production than loss with time. Soil texture also plays a role in the retention of SOC. Clay soils have the ability to retain organic C by the process of adsorption and soil aggregation, decreasing the gaseous loss of C. The total SOC content tends to increase with clay content while it decreases with temperature due to increased rates of microbial activity and organic matter decomposition (Jobbagy and Jackson, 2000). On the other hand, SOC tends to decrease on sunny slopes due to an increase in microbial decomposition with an increase in temperature.

In a study conducted by (Jobbagy and Jackson, 2000), the percentage of SOC was determined in the top 20 cm of a soil profile. The results were as follows; 33% shrublands, 42% grasslands, and 50% for forests. Below 20 cm, there was a variation in the percentage of SOC. The variation in SOC was from differences in root systems of plant types within a given soil, as well as climate and land use. However, a study conducted by Jin et al. (2013) concluded that the SOC storage was significantly higher in grasslands than in the forestland, with a difference of 15 Mg ha⁻¹, and the SIC grasslands was lower than that in the forestland, as much as 39 Mg ha⁻¹ (Jin et al., 2013).

When looking at the SOC distribution with depth, there was a greater association with vegetation than with climate (Jobbagy and Jackson, 2000). The deeper profile of shrublands had a greater SOC content compared to the grassland and forestland soils. The amount of SOC in the second and third meters of shrublands was 77% of that in the first meter; in forests 56%, and grasslands 43% (Jobbagy and Jackson, 2000). Therefore, there was a greater % of SOC deeper within the soil profile of the shrublands compared to the grasslands and forest land. On the other hand, when looking at the total SOC, there was a greater correlation with climate. They concluded that the significance of these controls changed with a change in depth, with climate having a greater impact in shallow layers while clay content as a primary control in deeper layers. This is possibly because of the increasing percentages of slowly cycling SOC fractions at deeper within the soil profile.

The type of vegetation has a greater influence than the average annual precipitation for a given climate. According to (Jobbagy and Jackson, 2000), a higher percentage of SOC was always deepest in shrublands, intermediate in grasslands, and shallowest in forests for a given climate. Therefore, the shoot/root proportions within a given volume, combined with vertical root distributions, have an effect on the distribution of SOC with depth (Jobbagy and Jackson, 2000). Because of this, the depth of sampling is crucial when estimating global SOC. The global SOC in the top 3 m of soil was estimated at 2344 Pg C, which was 56% more than when measuring the first meter (1502 Pg C), (100-200cm) 491 Pg C and (100-200 cm) 351 Pg C. The biomes with the greatest amount of SOC within the first 3 meters were tropical evergreen forests (158 Pg C) and tropical grasslands/savannas (146 Pg C), with the differences in amounts suggesting that plant functional types influence SOC distributions with depth in the soil (Jobbagy and Jackson, 2000). Depending on the depth and vegetation, current SOC calculations may

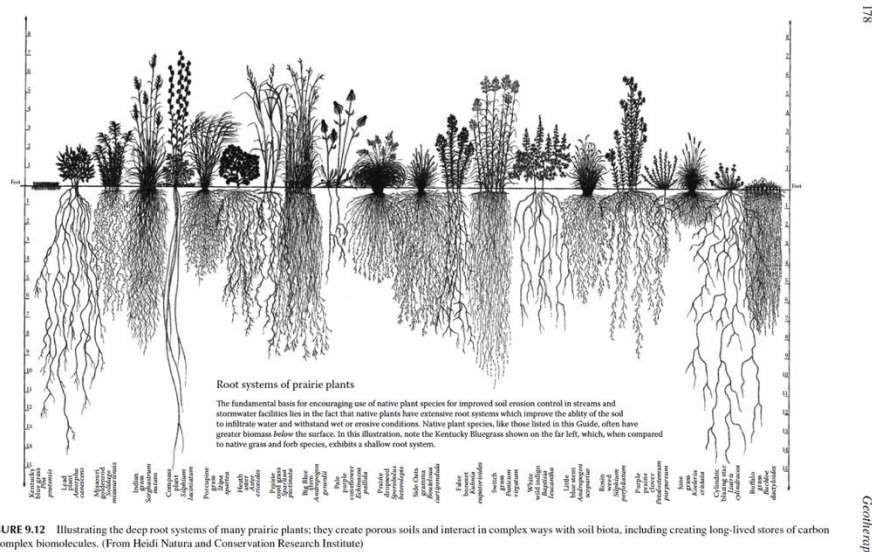


FIGURE 9.12 Illustrating the deep root systems of many prairie plants; they create porous soils and interact in complex ways with soil biota, including creating long-lived stores of carbon in complex biomolecules. (From Heidi Natura and Conservation Research Institute)

Figure 5.2 Root System of Prairie Plants (Graphic by Seth J. Itzkan; USDA/Agricultural Research Service, Glomalin is key to locking up soil C, Science Daily, June 16, 2008, <http://www.ars.usda.gov/is/pr/2008/080617.htm>.)

5.2 SIC and SOC

The chemical and physical processes of soil formation are the driving factors for the spatial pattern of SIC within a given soil profile, whereas the biotic processes are they key controls for the spatial patterns of SOC within a given soil profile (Shi et al., 2012). SIC is mainly controlled by the soil pH or factors that result in soil acidification and other processes driven by changes in pH such as the dissolution of minerals (Shi et al., 2012). The formation of SIC involves the weathering and dissolution of Ca/Mg-bearing silicates and the subsequent precipitation of carbonate minerals (calcite and dolomite). There is no net C storage with the dissolution, yet during the precipitation reaction atmospheric CO₂ is consumed resulting in C sequestration (Tamir et al., 2012). In model based on the acidification rates of soils under grasslands in the future and acidification of soils in croplands of the past, show that soil acidification will ultimately result in a decrease in SIC, with a 30 % and 53 % reduction in SIC respectfully (Shi et al., 2012). Jin et al., 2013 concluded that the biogeochemical characteristics

of the grassland favored the formation of bicarbonate, yet upon dissolution, the SIC was likely removed from the system in the form of DIC. However, the decline in pH also inhibits microbial decomposition; thus, the loss of soil C should not be significant in these soils (Shi et al., 2012).

Based on the current published literature, SOC seems to be the primary focus when it comes to soil C sequestration. However, the inorganic soil C pool should not be disregarded as a potential C sink. This is because depending on the parent material, OM inputs, soil organisms and climate, the SIC and SOC pools vary. For example, in arid and semiarid climates it has been reported that the SIC pool can be as much as 2-10 times larger than the SOC pool (Eswaran et al., 2000), and when combined, these regions cover as much as one-third of Earth's surface (Eswaran et al., 2000). Feng et al. (2001) reported that soil C stocks in desert regions of northern China had 1.8 times more SIC than SOC. Additionally, the SIC of both the grasslands on the Tibetan Plateau and the Chinese Loess Plateau were 2.1 times more than the corresponding SOC stock (Tan et al., 2014; Yang et al., 2010). Therefore, although the SIC pool may be small in proportion to many SOC pools, its contribution of storing C within a given soil may be significant. Thus, monitoring the SIC stabilization and accumulation, as well as the vertical distribution is crucial when accounting for total soil C. However, there is little information on the vertical variation of SOC and SIC with soil depth, yet this knowledge is imperative to making reliable predictions of soil C dynamics and potential storage capacities (Zhao et al., 2016).

5.3 Vertical distribution and transformation of SOC and SIC under different types of vegetation

A study published in 2016 examined the vertical distribution and transformation of SOC and SIC under different types of vegetation and slope aspects in the Zhifanggou Watershed on the Loess Plateau (Zhao et al., 2016). In the July 2011 study, 68 soil profiles were investigated:

30 soil profiles under forest (*R. pseudoacacia*), 13 soil profiles under shrub (*C. korshinskii*), and 25 soil profiles under grass (*S. bungeana*, *B. ischaemum* (L.) Keng, and *Carex lanceolata*) (Zhao et al., 2016). After removing the litterfall, the soil samples were collected using a 5-cm diameter soil auger at 10 cm intervals from 0 to 60 cm and at 20 cm intervals from 60 to 200 cm (Zhao et al., 2016). Then, samples were taken of each plant species (forest, shrub, and grass) for the shady and sunny slopes). After processing the samples in the lab to determine the C content, two fractions of SIC were obtained; lithogenic inorganic C (LIC), from parent material, and pedogenic inorganic C (PIC), which is from the dissolution and precipitation of secondary minerals (Zhao et al., 2016).

Results from the study showed that initially there was an accumulation of organic C as there was a decrease in the C/N ratio with litter fall additions, showing that low C/N ratio of plant litter is favorable to the formation of SOC (Zhao et al., 2016). Lower C:N or higher levels of N, stimulated microbial activity and increased rates of decomposition into SOM. Shrubs have the greatest, followed by forests, and then grasslands, just as the study published by Jobbagy and Jackson. However, on sunny slopes, the addition of organic C from litter fall did not result in high amounts of SOC formation, possibly due to the lower water content and increased rate of decomposition due to direct sun and temperatures.

The opposite was found for SIC, with higher amounts of SIC in the sunny slopes (Zhao et al., 2016). Thus, a lower activity in soil microbes on the sunny slopes results in relatively low SOC formation, and that increased microbial activity leads to decreased SIC. The increase in

microbial biomass mineralizes the unstable organic C producing more CO₂. However, the dissolution of CO₂, and the formation of bicarbonate can promote the precipitation of CaCO₃ (Zhao et al., 2016). SIC increased in the top 0–50 cm of soil, and looking at the entire profile (0–200 cm) of the sunny slopes, shrubs had the highest SIC content, followed by grasslands, then forest. However, the SIC on the shady slope was significantly different. The soil water content was also higher (0–30 cm) in the shady slopes, with grasslands having the greatest SWC, then shrubs, followed by forests. When looking at the soil profile from 30–200 cm, forest had greater SWC than shrubs. The higher SWC from 0–30 was due to higher root density, and the root length was a contributing factor when taking samples from the 30–200 cm depth.

They also found that shrub soils were inorganic C sinks because they contained the greatest quantities of Ca in the litter and the unstable organic C, leading to the precipitation of CaCO₃ from the decomposition of shrub litter. Additionally, the pedogenic carbonate that formed had a decreased rate of dissolution and precipitation due to low soil water content, and at the same depth, the SIC in the soils under shrub cover was found to be relatively higher when compared with forest and grass covered soils, making shrubs a possible inorganic C sink (Zhao et al., 2016).

Together, climate and vegetation affect the accumulation of SOC and SIC in a given soil. When looking at the three types of vegetation presented, it was the shrublands that were most advantageous for fixation of inorganic C (Zhao et al., 2016). Additionally, for all three types of vegetation, the SIC was negatively correlated with the soil water content and in the two slope aspects, making it clear that as the SWC decreased, so did the rate of dissolution and precipitation of the pedogenic carbonate in the soil profiles (Zhao et al., 2016). Therefore, when considering soil as a potential sink or source of C, not only does that type of vegetation and

climate need to be considered, but the SIC content and potential of a soil to sequester SIC needs to be taken into consideration. This fraction tends to be overlooked, yet although it may be a small when compared to SOC, SIC can play a role in Global C Sequestration.

Recently, Myers et al. (2011) presented such as a model for identifying peak functions for continuous modeling of the vertical variation of soil properties. These continuous soil prediction methods can be applied vertically (along soil profiles) or horizontally (across landscapes) to quantify soil patterns across large regions. However, the majority of the existing soil C maps are often based on data that poorly reflects the C pool of deeper soil horizons, and the effects of land use changes on deep C stocks have been poorly addressed. Thus, the understanding of SOC stabilization processes is incomplete, and there has yet to be a general agreement on soil C fractionation methods to estimate the degree of stabilization. Nevertheless, there is a need for the development of a model that is used globally to account for the vertical distribution of SOC within a soil profile that can be used for large-scale estimations for accurate quantification of SOC stocks.

Chapter 6. The importance of soil sampling depth for accurate account of soil organic C sequestration, storage, retention and loss.

The precise quantification of soil C stocks is crucial for making predictions and decisions for using the soil C pool in counteracting climate change. However, many of the previous SOC stocks were collected to depths of 30 cm, and it has been found that a large margin of SOC is present below 30 cm has been unaccounted for, underestimating soil's capacity to store and retain C (Geotherapy, 2015). The organic C within the SOM represents approximately 51% of the Global Terrestrial C Pool, with a majority (75%) of SOC located within the subsoil (down to 3m) (Bohn et al., 2015). According to Geotherapy (2015), the SOC within the upper 30 cm of a

soil profile is estimated to have, at most 684 to 724 Pg C and between 1468 to 1548 Pg C when measuring to a depth of 100 cm. And when measured to 200cm, it was found that the soil profile contained as much as 2376 to 2456 Pg C. Therefore, soil sampling depth must be considered when determining total SOC.

SOC Estimations			
Depth (cm)	Batjes 1996	Lal (2004)	Hiederer and Kochy (2011) (2469 Gt)
0-30	684 to 724 Pg	2500 (Gt) SOC 1550 Gt SIC 950 Gt	967.3 Gt C
0-100	1468 to 1548 Pg		1502.2 Gt C
0-200	2376 to 2456 Pg		(1.5 X SOC topsoil)

Table 6.1 SOC Estimations (Batjes, 1996; Lal, 2004; Hiederer and Kochy, 2011)

Many factors dictate the many changes in SOC stocks (Olson, 2013). SOC stocks and the fluxes within the soil C pool are ultimately governed by soil forming factors (PM, topography, climate, biota, and time). However, many other factors can impact the C stocks as well; such as management practices such as tillage and different land use and land changes, and even the drainage passages. In the 20-year study comparing no-till and moldboard plow and chisel plow, it was found that root systems contain a significant contribution to the total SOC present within soil (Olson and Al-Kaisi, 2014). Samples were taken at 5 cm intervals for a total of 75 cm. Then, SOC storage, retention and loss were determined for the 0–5 cm, 0–15 cm, 15–75 cm and 0–75 cm layers. The results were that no-till retained more SOC than the conventional tilling treatment with the upper 20 cm of the soil profile, but the SOC stock of the 20–35 cm layer no-till system was lower than the conventional tilling treatment (Olson and Al-Kaisi, 2014). However, it is important to remember that the estimations of SOC stocks vary due to differences in sampling protocol (Olson and Al-Kaisi, 2014), and even though no-till has been suggested and is a widely

accepted management practice, results are inconsistent, as they vary between a significant increase and decrease in SOC stock estimations. Additionally, the use of conservation tillage does not always result in increased SOC storage. When sampling soil for future SOC stocks estimations, the depth of soil sampling must include the entire root zone (Olson and Al-Kaisi, 2014). Therefore, there is a need to develop a unified protocol for soil sampling collections for determining precise SOC Stock estimations, including both soil depth, soil forming factors in a given location, and management practices. There is also a need for the development of a matrix including soil types, vegetation type or class, management practices, and land use practices that can be used to quantify SOC stocks. Furthermore, soil C variability with depth needs to be better represented (McBratney et al., 2015), and the development of models representing the many changes soil C in relation to management practices within the entire soil profile (McBratney et al. 2015).

Chapter 7. Understanding biogeochemical cycles, biodiversity, and the many ecosystem services provided by soils to achieve soil C sequestration

The soil C pool and the ecosystem services it provides play a pivotal role in protecting global biodiversity and climate. Soil acts as a plant medium, water filtration system, a foundation for infrastructure, and habitat for voluminous amounts of organisms, continuously cycling matter. The processes undergoing within a soil are fundamental ecosystem services, with soil formation itself being the bolster to such services. A full understanding of soil biodiversity, its involvement within the global biogeochemical cycles, and the essential ecosystem services it provides is critical, and current research of the SOC processes at the large scale (biosphere to biome scales) are not well understood (O'Rourke et al., 2015). Nevertheless, very element and

function of this vital system must be identified and understood for future decisions implementing a climate change mitigation plan involving soil as a potential C sink. Therefore, future research needs determine the underlying ecological processes that result in changes in SOC in order to understand continental and global soil patterns, which will require a thorough assessment of the factors many that may affect the spatial behavior of soil and ecological variables observed.

7.1 Regulating and Supporting Services

Such ecosystem services include regulating and supporting services. Regulating services provide benefits through the regulation of ecosystem processes, whereas, supporting services are essential ecosystem services for the production of all other ecosystem services (Smith et al., 2015). The fundamental supporting services that this system provides include soil formation, nutrient cycling, water cycling, primary production, and habitats supporting species diversity. Thus, knowledge of these supporting services and the processes involved are prerequisite to making informed decisions of potential regulating services, such as C sequestration and climate regulation. Therefore, it is imperative to identify the current gaps and challenges in soil research to make promising decisions and recommendations of management practices that would improve soils health and its role in ecosystem services. Such gaps within this interconnected system involving the cycling of C, nutrients and water, and their role in providing habitats for soil organisms and genetic diversity (Smith et al., 2015). However, although there are gaps that need to be filled, the current plethora of knowledge the scientific community has acquired about soils in the past few decades is enough to start making changes that can improve soils globally.

Many soil scientists have devoted their careers to understating the dynamic system of soil and its role in the global earth system. However, communicating and sharing this knowledge

with soil managers and policy-makers, for implementing the best practice is an important challenge. This problem can be overcome by raising awareness of the many ecosystem services bolstered by soils, and the value this resource provides. Followed by the establishment of methods and steps for utilizing this scientific knowledge to bring about a more sustainable use of soils. Safeguarding this valuable complex system, and its function and services within the Global Earth System is a crucial element in sequestering C while stabilizing climate.

Soil is an important component to the environment, as it is the interface between the atmosphere, biosphere, geosphere, and hydrosphere. Soil is the largest terrestrial C reservoir within global C cycle, continually undergoing chemical and physical processes exchanging and cycling C at various turnover rates within and between through the Earth's spheres. The interconnection of all of earth's spheres plays a significant role in soil formation. In turn, the properties and processes of a given soil impact nutrients for plant growth and hydrologic conditions such as water quality and plant available water, all of which are closely related to SOC, which in return affects species diversity and activity, soil quality, NNP, and water quality.

The amount of C within the soil pool (~1500–2400 Pg) is greater than the atmosphere (590 Pg C) and terrestrial vegetation (350–550 Pg C) combined (Schlesinger and Bernhardt, 2013; Ciais et al., 2013). However, soil C stocks are in constant flux, controlled by the amount and type of organic matter inputs, the efficiency of microbes to utilize the SOC, and the capacity of the soil to retain SOC by physical or chemical stabilization (Cotrufo et al., 2013).

The soil C pool can be divided into two major components; organic and inorganic soil C. Most of the current research focusses on the organic C pool, as it makes up for as much as 1500–2000 Pg C to 1 m depth, and as much as 2500 Pg to 2 m (Batjes, 1996; Govers et al., 2012);

Schlesinger and Bernhardt, 2013). Whereas the inorganic C pool contains approximately ~ 750 Pg C to a depth of 1 m (Batjes, 1996), with total SIC estimated at 940 Pg C (Monger, 2015).

The boreal soils under permafrost conditions have been found to have high values of SOC. This is because microbial decomposition is inhibited under certain environmental conditions such as low temperatures, low pH, and anaerobic conditions of cold climates or waterlogged soils. The highest amount of C is found in the top 30cm, where litterfall is deposited, yet, there is a large portion of C below 30 cm that is often overlooked when making global estimations. In 2009, Tarnocai et al. reported that 61 % of soil C within the northern circumpolar permafrost region was stored below 30 cm (Tarnocai et al., 2009). Some soils have a greater ability to store C even though the land area coverage they reside in are relatively small when compared to other regions comprising the total global land coverage. Therefore, the lack in land area coverage does not reflect the potential of these soils to act as soil C sinks. For example; 3 % of the land area is covered by peatlands containing only about 500 Pg C in organic-rich deposits ranging from 0.5 m up to 8 m deep (Gorham, 1991; Yu, 2012). Also, some soils contain a greater amount of inorganic C, such as some arid and semi-arid soils derived from carbonate-bearing parent materials, where the dissolution and secondary precipitation of carbonate minerals in the subsoil can accumulate. Yet, changes of the inorganic C pool are slow and their role in ecosystem services is not as significant as the SOC pool. However, although the SIC pool is often overlooked when viewing soil C on a global scale, there has been recent studies showing that the addition of finely grained silicates can enhance carbonate precipitation, removing CO₂ from the atmospheric pool in the process. Nevertheless, both soil C components are involved directly or indirectly in the ecosystem services soils provide.

7.2 *Soil Formation and Ecosystem Services*

The process of soil formation is an ecosystem service, undergoing transformations, translocations, losses and additions, cycling C, essential plant nutrients and water, all while providing a plant medium and habitats for soil organisms. The stabilization of soil C requires a net balance between C inputs and outputs. Soil C is lost mainly through microbial decomposition or mineralization, followed by leaching of dissolved C, and carbonate weathering (Schlesinger and Bernhardt, 2013; Smith, 2012), whereas NPP and the subsequent litter fall are the primary inputs. And, depending on the response of a given soil system to climate and land practices, the SOC stock can shift, either increasing or decreasing. Additionally, soil C varies with depth within a given soil profile, with the topsoil having a rapid turnover rate, whereas soil C associated with specific mineral components in the subsoil C pool can reside in the soil for extended periods of time, for hundreds to thousands of years (von Lützow et al., 2008; Rumpel and Kögel-Knabner, 2011).

7.3 *SOM and Ecosystem Services*

Soil organic matter is an important element of the supportive ecosystem services within a soil. Soil high in SOC possesses chemical and physical properties that enhance nutrients, soil water holding capacity, the formation of aggregates, and sorption of organic or inorganic pollutants, creating a habitat that supports a diverse assemblage of soil organisms. Additionally, management practices that improve SOM promote these supportive services while increasing SOM and soil health.

The C within plant roots accounts for most of the SOC, as it is buried, which slows the rate of oxidation and reduces microbial access (Rasse et al., 2005). The soil pool is a complex

biogeochemical mixture, comprised of water, air, inorganic minerals, and most importantly OM in all stages of decomposition. SOM that has undergone partial microbial decomposition can then become protected from further decay as it is bound to minerals or when it is physically occluded into aggregates, inhibiting microbial access, thus slowing the turnover rate. Although some C compounds are more resistant to decomposition, surface additions are more prone to degradation as they are exposed; thus, this portion has little influence on the longevity of soil C residence time (Thevenot et al., 2010). For that reason, the location SOM within a soil matrix can strongly influence the rate of turnover.

The associations between SOM and soil mineral components have great control of the turnover rates, and the efficiency of microbes to use plant inputs and the subsequent interactions with soil minerals has a significant influence on the SOM stabilization (Cotrufo et al., 2013). For example, peats have high OM content because waterlogging of these soils and anaerobic conditions slow down biological activity and decomposition. Yet, all SOM will ultimately result in mineralization in aerobic conditions, releasing CO₂ once again.

The release of CO₂ following SOM mineralization, as well as from rhizosphere respiration and inorganic C weathering, accounts for 60 Pg C that is released back into the atmosphere, making it the greatest terrestrial flux of CO₂ to the atmosphere (Smith et al., 2004). A flux significantly larger than anthropogenic CO₂ emissions from fossil fuel burning and land use change (1.1 Pg C yr⁻¹) (Ciais et al 2013).

7.4 *Climate and Ecosystem Services*

Both, the temperature and annual precipitation of a given climate also impact the rate of turnover. Cold, dry, and anoxic conditions that inhibit microbial SOM decomposition result in

SOM accumulation. And, when water is not a limiting factor, rates of microbial decomposition increase with an increase in temperature. However, the temperature sensitivity of SOM varies due to the chemical and physical protection of organic matter in soil (Conant et al., 2011; Zheng et al., 2012). Well-aerated soils promote microbial activity, yet the rate of decomposition decreases as soils become drier. On the other hand, flooded (saturated) soils have restricted aeration that results in lower rates of organic matter decay, thus tend to accumulate SOM. High precipitation, however, may lead to C loss from the soil profile as infiltrating water and leaching removes dissolved and/or particulate organic matter, and by surface runoff and soil erosion. Additionally, the rewetting of soils after drought conditions can increase microbial activity, accompanied by an acceleration of CO₂ emissions (Borken and Matzner, 2008), whereas drought conditions in naturally anaerobic soils, such as peat, may increase decomposition (Clark et al., 2012; Freeman et al., 2001). Drought can also affect the quantity and quality of the composition of plant litter, as well as enzymatic activity within the rhizosphere (Sanauallah et al., 2011), both resulting in a reduction of soil C.

7.5 *Soil Nutrients and Ecosystem Services*

Soil functions as a plant medium supporting primary production, which in return provides the foundation for food and stored energy to be transferred within the organisms of an ecosystem. Lack of nutrients within a soil can also impact the soil system, decreasing plant productivity, as plants are forced to compete with soil organisms for nutrients. When nutrients are limited, it has been shown that additions of N and/or P have increased rates of C accumulation (Aerts et al., 1992; Turunen et al., 2004; Olid et al., 2014). However, additions of N and P must be within the tolerance levels of sensitive plant species. Concentrations above the

plant tolerance level may lead to a decrease in C as it impacts plant growth and function.

Reductions in NPP reduce the continued C inputs into the soil system, inhibiting the regulating service of C storage to reduce atmospheric C. Although excess N can increase new growth in the top of the plant, it deprives the low portion of the plants of nutrients leading to N induced stress. Root growth stunting can destabilize the plant, making it fall over, eventually subject to microbial decay. Excess N can also be leached from the soil system, increasing concentrations downstream which may result in eutrophication. Excess N can take away water from the plant, leaving behind salts that accumulate over time in climates that have lower rates of precipitation, resulting in plant dehydration, yellowing, and wilting of leaves. Excess salts may also inhibit microbial activity, reducing microbial populations that fix atmospheric N for plant uptake, as well as impact soil respiration, residue decomposition, nitrification, and denitrification.

Therefore, the cycling of C, N, and P in soils is tied to the fixed stoichiometry requirements of plants and microbial organisms. The ratio of C:N:P for specific plant growth and microbial activity needs to be more understood to properly identify management practices that result in improved nutrient use efficiency and productivity (van Groenigen et al., 2010; Venterea et al., 2011). Nevertheless, nutrient additions can increase or decrease soil C storage, as well as negatively affect the regulating services of soil, air and water quality (Smith et al., 2013). The change in soil C is governed by the initial SOM stoichiometry, capacity of minerals to preserve microbial products preventing further decomposition, and the simultaneous effects on SOM inputs and plant productivity (Smith et al., 2013). In order to sustain the many ecosystem support services soil provides, soil fertility and cycling of nutrients needs to be preserved and restored where needed. The response of ecosystems to fertilization needs to be well understood in order to effectivity and reliably implement management practices that not only support plant productivity,

but also preserve or enhance SOM stocks, as well as reduce nutrient loss to the atmosphere or to water resources that contribute to the valuable supporting ecosystem services.

7.6 *Soil Texture and Ecosystem Services*

Soil texture is also an important factor controlling the quantity and composition of soil C. The physicochemical protection of SOM due to mineral associations can lead to reduced microbial accessibility, thus increasing C storage. For example, organo-mineral associations such as iron oxyhydrates coatings on soil mineral particles help stabilize C, contributing to a higher C storage (Song et al., 2012). Coarse or sandy soil textures may result in increased leaching of the fine OM particles and plant nutrients, and have greater rates of oxidation as they are exposed to oxygen and easily accessed by microorganisms within the matrix of larger pores. Thus, resulting in C and nutrient loss from the system, a reduction in plant productivity, and the accumulation of potentially harmful concentrations of nutrients in downstream aquatic ecosystem. Additions of OM, may alleviate this loss by the formation of aggregates, or possibly selecting plants that thrive in coarse textures that have an extensive root system for increased C storage.

7.7 *Bioturbation and Ecosystem Services*

Bioturbation influences the amount and nature of soil C. Biologic activity incorporates and transforms organic compounds into soil, which could result increased C storage. In a study reported by Mathieu et al., 2015, the maximum values of C with depth were found in soils with that had higher amounts of pedoturbation. Soil plant activity or deep rooting within some soils (vertisols, nitisols, ferralsols, and chernozems) had a greater amount of deep soil C incorporated within the soil, than in soils with lower levels of pedoturbation (podzols, cambisols, luvisols, and

andosols) (Mathiue et al., 2015). The plant roots coated in the symbiotic mycorrhizae hyphae extend out within the soil, and the digging of channels by earthworms facilitating in good soil structure, continuously mixing newly added OM into the existing soil matrix. Microorganisms transform OM into humus, and when they die, their remains contribute to the SOM pool.

Vegetation also has a significant influence on the OM inputs and microbial activity within a soil system. The type of C compounds from plants inputs influence the labile fraction of SOM, which in return affects microbial efficiency and rates of decay. Therefore, soil organisms and the processes in which they undergo are critical factors in sustaining supporting and regulating ecosystem services as they indirectly control the net balance of SOM by their influence on soil water, structure, labile C inputs, pH, and nutrient cycling.



Photo 7.1: USDA NRCS

7.8 *Soil Water and Ecosystem Services*

The cycling of nutrients and water are fundamental and possibly the most important ecosystem service soil performs. Soil is a biogeochemical matrix, with all spheres interacting together, cycling matter in the solid, liquid and gaseous phases. The organic matter and mineral soil particles interact with the soil solution within a given soil texture and structure, with hydrology being a driver for seasonal and inter-annual variability of SOC concentrations and export (Mattsson et al., 2014). Together, OM and soil mineral constituents aid in nutrient and water retention, exchanging ions with the soil solution, while acting as a water purification

system. This ecosystem service is crucial in providing valuable water resources around the globe. Precipitation and infiltration must exceed evaporation, leaching and runoff for water to be stored within a given soil. Porous soils have high infiltration and permeability due to coarse texture, leading to leaching and drained soils. Finer textured mineral soils have high nutrient and water retention, yet without OM, soil structure will be weak, lacking in soil aggregates, leaving the soil unable to act as a water filter. Additionally, deforestation and improper management practices can affect soil structure, reducing infiltration, water retention, and water quality. For example, overgrazing can result in surface erosion and runoff, and excessive tillage of fragile lands compact soils, deteriorating soil structure while enhancing that oxidation of OM within the topsoil.

In 2012 soil C study in Florida, it was found that the hydrological patterns of a given region were the primary control of total soil C (Vasques et al., 2012). This is because of the influence of with water as a soil forming factors controlling the processes such as organic matter decomposition, transformation, and accumulation in the soil (Cao,2015). Vasques et al. (2012), concluded that the soil available water capacity at local and regional scales are closely related to the spatial dependence and patterns of soil C (Cao,2015). However, in a 2015 study in Florida, by authors Xiong et al. (2015), it was found that there was a large spatial variability of SOC in both long range and short range. The variation was possibly due to factors such as soil moisture regime, but it could not be explained by the available environmental factors (Xiong et al., 2015). They also concluded that the variation in SOC from both large and small ranges suggested that the soil forming processes in the topsoil were mainly driven by soil water gradients and soil-specific properties such as texture and structure (Cao,2015).

The different drainage classes within a given region resulted in variation of SOC stocks (Cao,2015). Lower drainage areas tend to store more water, promoting higher productivity for an increase in C input than in well drained areas or areas of high infiltration rates that did not retain enough water for plant growth due to rapid draining and leaching of nutrients and OM (Cao, 2015; Vasques et al., 2010). In a study by Cao (2015), concluded that there were larger values of SOC $>40 \text{ Kg m}^{-2}$ in in very poor drained soils or seasonally waterlogged soils of Florida. The waterlogging produces an anaerobic environment that inhibits decomposition and promote C accumulation. It was also found that the available water capacity, drainage classes and hydrologic groups for a given mean annual precipitation are indirectly related to the control of hydrologic conditions of a soil site, thus impacting soil C dynamics (Cao, 2015), supporting the claim by author Nemani in 2002 that water and C cycles are strongly coupled. However, although water is an essential factor in soil formation and plant productivity, other environmental variables had a strong influence on the SOC stocks (Cao, 2015). Nevertheless, SOM and soil water retention and structure are directly related, all of which have an influence on the formation of SOC. Thus, increasing SOM, while properly implementing effective management practices can improve soil hydrological functions while storing C to offset GHG emissions.

Although practices for maintaining supportive ecosystem services are well known, their application is not universally implemented, and poor management leads to a loss of function, inhibiting soil the soil to act as a natural filtration system. As the climate continues to change with increased precipitation and/or droughts, soils functions will be stressed, possibly requiring restoration management practices. Therefore, soil must be managed appropriately to assure the preservation of these vital ecosystem services it provides. This would require future research to

focus on the interactions in current and potential future conditions, to ensure the preservation of soil, its services, and potential to regulate climate change.

7.9 *LULCC and Ecosystem Services*

The interconnected relationship between organic matter and soil C, nutrients, water and biota, is indivisible. Thus, converting natural land to agricultural would change the balance between these factors, resulting in a shift back to a steady state. A number of studies (Wei et al., 2014; Guo and Giord, 2002; Don et al., 2011) show that the conversion of natural systems to agricultural that C is lost from the system, as much as 25%–30% of the SOC in the top meter to be lost (Post and Kwon, 2000; Guo and Gifford, 2002; Murty et al., 2002; Don et al., 2011). While, other studies reported that when converting forest to pasture, there was C gain (Guo and Giord, 2002), while others reported C loss (Don et al., 2011). Additionally, the restoration of surplus or former croplands can help to alleviate the loss from land use and change, and increase soil C stocks, nutrients, biodiversity, and water quality by the use of improved agricultural management practices, while demonstrating that natural vegetation restoration and tree plantation are two important means to remediate degraded ecosystems, both of which significantly promote soil C storage (Houghton et al., 1999; Lal, 2004b; Woodbury et al., 2007; Piao et al., 2009; Huang et al., 2012).

A change in management practices for land use can also promote SOC accumulation or stabilization. Reduced tillage within the top 30cm of soil, and zero tillage has been found to increase soil biota while reducing the soil C turnover rate. Promoting the growth of perennial crops with large root systems reduces the need for annual tillage and can help replenish soil C in the depleted subsoil (Kell, 2012). During a period of fallow, maintaining ground cover through

the use of cover crops and improved residue management, as well as properly rotating crops, can improve soil C, prevent erosion, help in maintaining nutrients, all while supporting soil biota (e.g. Mbow et al., 2014). Additionally, the application of organic amendments, such as crop residues, manure, and compost can increase SOM, soil C, nutrients, water quality and biota (Gattingeret al., 2012; Lal, 2004; Smith, 2012). Moreover, the implementation of optimized nutrient management by accurately timing the application of fertilizers for when the plants are able to efficiently utilize the nutrients will reduce nutrient loss and downstream eutrophication while promoting increased production, which can lead to increased soil C. As can precision farming and establishing nutrient requirements for specific plant types to optimize yield while targeting specific plant needs. Water quality and soil organisms can also benefit from reduced applications of agrochemicals; however, pesticides and herbicides may be necessary to return the land back to production (Carlton et al., 2010, 2012). Conversely, draining of wetlands for agricultural will lead to the oxidation of SOM with a large loss in soil C, and hindering the process of denitrification and the soil's ability to act as a natural water purification service. Therefore, the soil environment and the ecosystem services it provides will be directly impacted as a result of land use and land change, and the changes in soil C stocks are dependent on land-use shifts, climate change, and other environmental or human-induced stressors.

7.10 Conclusion of Soil and Ecosystem services

Soil acts as an interface at which all of Earth's spheres are interacting, with soil functioning as a medium to store and cycle water and nutrients, while offering many valuable supportive ecosystem services. The identification and quantification of the sources and sinks within the soil C pool and the many ecosystem processes it plays within the global earth system

is necessary for counteracting potential future imbalances within this vital system and the many ecosystem services it provides. Supportive services such as soil formation, nutrient and water retention, that together enhance primary production. Soils also provide a habitat supporting a diverse community of organisms that play critical roles in sustaining soil and many other ecosystem services. Services that are fundamental in potential regulating services soils' have to offer, specifically, C sequestration to reduce atmospheric C concentrations resulting in climate change. Agricultural practices and their benefits or detriments must be identified for all types of soils. Then, methods of communicating this knowledge to the scientific community and policy makers need to be established in order to implement these best management practices for specific agricultural needs. Although there have been many recent advances in the methods for estimating SOC stocks, there is still a need for a global scale synthesis, as well as a need to identify and understand the functional roles of distinct types of organisms found in different soils to make reliable predictions of their vulnerability to future change. Additionally, even though management practices that support soil C, nutrients, water and biota have been established, balancing the trade-offs between different ecosystems services is a challenge. Therefore, continued research to understand fully the relationships between the many facets of soils and the array of ecosystem services they underpin, is imperative to ensure its preservation and potential role in future climate change mitigation. Research gaps based on the uncertainty of the behavior of soil C need to be filled. The use of different models with dramatically different predictions of future climate trends depending on the representation of ecosystem C (Friedlingstein et al., 2006)

Ecological interactions between plants and microorganisms play a significant role in the SOM stabilization and destabilization (Averill et al., 2014), however, there needs to be more research identifying the interactions and their magnitude in changing the amount SOC within the

terrestrial C pool and relationship with the Global C cycle. Soil and ecological processes are interrelated related, and the wide scale spatial and temporal distributions have a great influence on these processes involved within the soil and global earth system. Increasing the current understanding the dynamic system of soil to develop insight into biogeochemical processes and its interactions within and among earth's systems would be advantageous for future predictions in potential human-induced disruptions or changes of SOC. Thus, there is a need to develop protocol and policy derived from an emergent of techniques to update our understanding soil data, involving the spatial behavior of soil and ecological variables. This requires that future research is needed to focus on the underlying ecological processes, as well as a full assessment of the many factors that may affect soil C observations and estimations of changes in SOC pool.

Chapter 8 Potential Solutions to Increase Soil C Stocks

8.1 Identifying and reversing specific Land Use and Land Coverages Changes that result C loss as a potential solution to increase SOC

In order for soil to offset C emissions, the C inputs must be equal or greater than additional C emissions released back into the atmosphere. In 2012, the emissions from fossil fuels was reported to be about 7.8 (± 0.4) Pg C/ year, with an additional net flux of 1.0 (± 0.5) Pg C/year from LULCC (Houghton et al., 2016). And, according to the NOAA measurements from 2000–2009, the annual accumulations of C into the atmosphere averaged 4.0 (± 0.1) Pg C/year (Houghton et al., 2016). The offset in emissions was contributed by global oceans uptake at 2.4 (± 0.5) Pg C/year, and terrestrial ecosystems, not taking into account of LULCC, taking in about 2.4 (± 0.8) Pg C/year (Houghton et al., 2016). This suggests that an increase in soil C storage by proper management practice in LULCC could further alleviate the current 4 Pg C released into

the atmosphere each year. Thus, there is a need for continued monitoring of soil with changes in LULC to have a full understanding to the capacity of soil C storage and to identify areas that have yet to reach the capacity. However, this would take a global effort, implementing site specific policy and regulations to successfully achieve this goal.

Many studies have concluded that LULCC are main factors affecting SOC stocks (Guo and Gifford, 2002a; Munoz-Rojas et al., 2011; Searchinger et al., 2008; Wang et al., 2011). Land use and change results in changes in biomass, vegetation, and disturbs soils, which can result in a loss of soil C and other nutrients, changes in soil properties, as well as changes to above- and belowground biodiversity (Smith et al., 2016). Soil formation and the biochemical alteration of litter fall transforming into the SOC pool can take several years, decades, or even centuries to accumulate, whereas the rate of SOC loss can be easily accelerated due to anthropogenic disturbance, change in land use, and poor management practices. Land use change can result in rapid loss of soil C, as well as increase C emissions. For example, The IPCC (2007) estimated emissions from deforestation in the 1990s to be at 5.8 GtCO₂/year (IPCC, 2007). In 2010, Friedlingstein et al., it was reported that from 2000 to 2009, there was approximately 1.1 ± 0.7 Pg C yr⁻¹ annual loss of soil C. However, emissions from LULC is the most uncertain component to the C budget. According to the IPCC's fifth assessment report, Working Group III, Chapter 11 (Smith P. et al., 2014), Globally, the agriculture, forest, and other land use (AFOLU) sector is responsible for about 24% (~10–12 Pg CO₂ /yr) of anthropogenic GHG emissions due to deforestation and agricultural emissions from livestock, soil, and nutrient management (Cao, 2015).

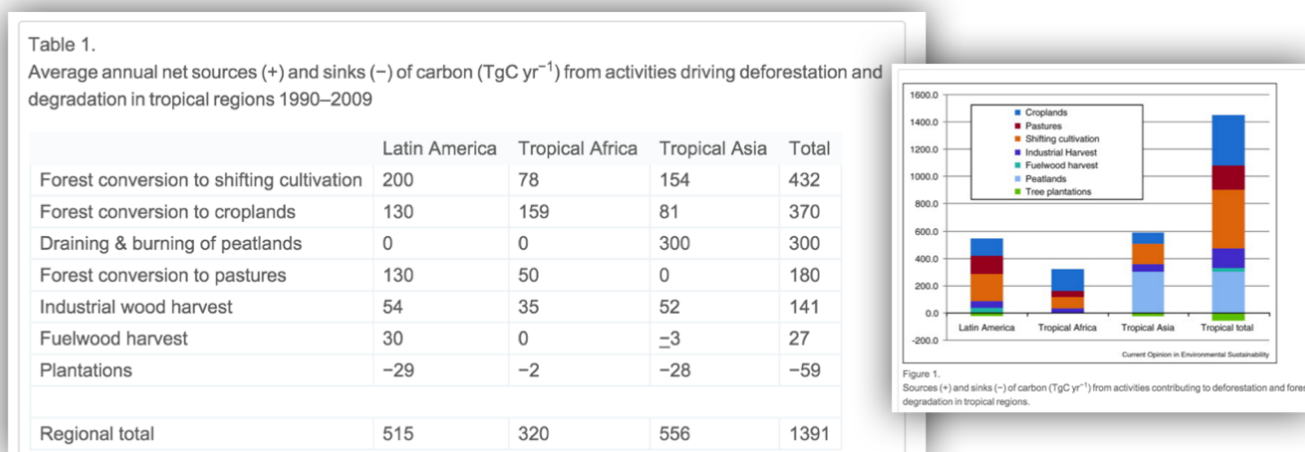


Table 8.1: Average annual net sources and sinks of C from deforestation and degradation in tropical regions (Houghton, 2012)

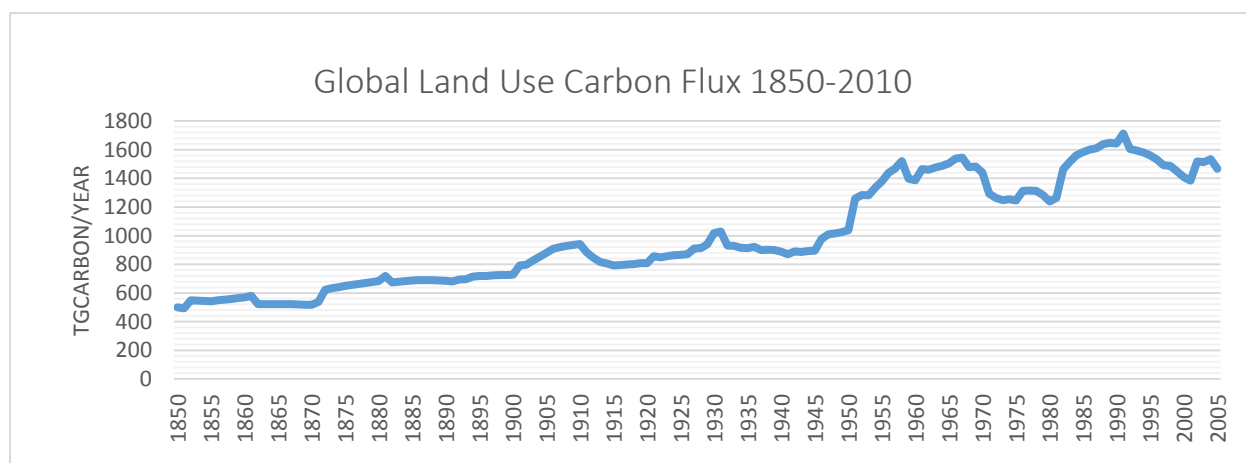


Figure 8.1: Global Land Use Flux 1850-2019

The natural soil state and the climate, type of vegetation, hydrology, topography and the nutrient environment that the soil is exposed to, influence a soil C stock capacity (Gupta and

Rao, 1994). Converting land from its natural environment can significantly affect the soil C stocks, shifting the balance between C sequestration and losses, yet this loss can be slowed by converting land back to grasslands, forests, and native woodland (Ostle et al., 2009). The Global Forest Resources Assessment 2010, estimated that the world's forests and other wooded lands store more than 485 Gt (1 Gt=1 billion tonnes) of C, 260 Gt in the biomass (53 percent), 37 Gt in dead wood and litter (8 percent) and 189 Gt in soil (39 percent) (FRA, 2015).

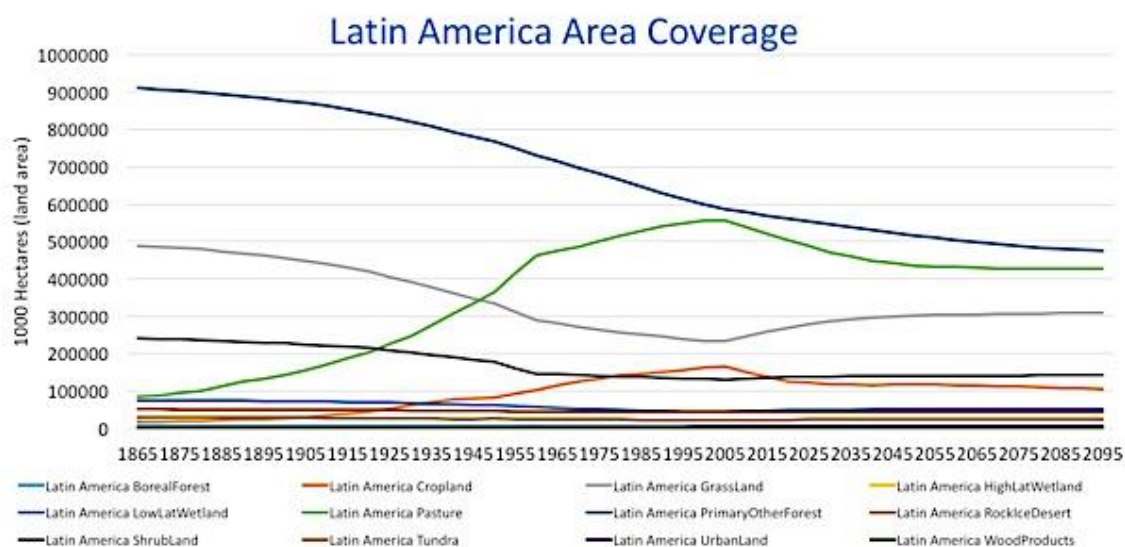
All soils have the ability to store C; however, depending on the LULCC, the capacity of C storage varies. Through sustainable management, planting and rehabilitation of forests, soil C stocks can be increased or at least conserved, while deforestation, degradation and poor forest management result in reduced C stocks (UNFCCC, 2016). From 2011-2012, there was an annual decrease of about 0.22Gt from the world forest biomass C stocks, mainly due to loss in the global forest area (UNFCCC, 2016). Nevertheless, not all changes in land result in C loss or soil degradation. Land conversions may actually benefit soil, yet having a full understanding of the climate, land, vegetation, soil, and management practices in place is necessary to make informed decisions about land use and potential land conversions that would result in soil C increases.

Source	Emissions Estimation	Location
Potter, 2009	0.6 Pg C / Year	Tropical Forests
Houghton, 2012	1.4 (± 0.5) Pg C yr ⁻¹	Tropical Rain Forest
Xiao-Peng Song et. Al, 2010	0.18 \pm 0.07 Pg C•yr ⁻¹	Annual C Emissions from Deforestation in the Amazon Basin

Table 8.2. Emissions from loss in forest coverage (Potter, 2009; Houghton, 2012; Xiao-Peng Song et. Al, 2010)

In a study by Ostle et al. (2009) it was reported that shifting native forests and croplands to grasslands can significantly increase SOC, (+8 percent), shifting cropland to plantation

increased SOC up to 18 %, and cropland to secondary forest had a 53% increase (Ostle et al., 2009; Stockman et al., 2013). However, there was no effect on soil C stocks when shifting native forest or grassland to broadleaf deciduous tree plantations, and when converting to pine or coniferous forest, SOC was reduced up to 15% (Ostle et al., 2009; Stockman et al., 2013). The same study reported that SOC stocks declined 10 soil % after a conversion from pasture to plantation forest, 13% when converting native forest to plantation forest, 42% for the conversion of native forest to cropland, and a 59% decline when converting grasslands to croplands (Stockman et al., 2013). Based on these numbers it can be said that when changing land use from cropland to pasture or cropland to permanent forest result in the greatest gains of SOC (Stockman al., 2013). Therefore, identifying and reversing specific land use changes that result in C loss, could potentially increase soil C stocks. Although, converting land back to original will increase C storage potential, the amount of time it takes to recover soil to the original SOC stocks due to disturbances in change inland use can take decades or even centuries (Guo and Gifford, 2002).



Reference: "Smith SJ, and AJ Rothwell (2013) "Carbon density and anthropogenic land-use influences on net land-use change emissions" Biogeosciences 10, 6323-6337, doi:10.5194/bg-10-6323-2013"

Figure 8.2. Latin America Area Coverage, Smith & Rothwell, 2013

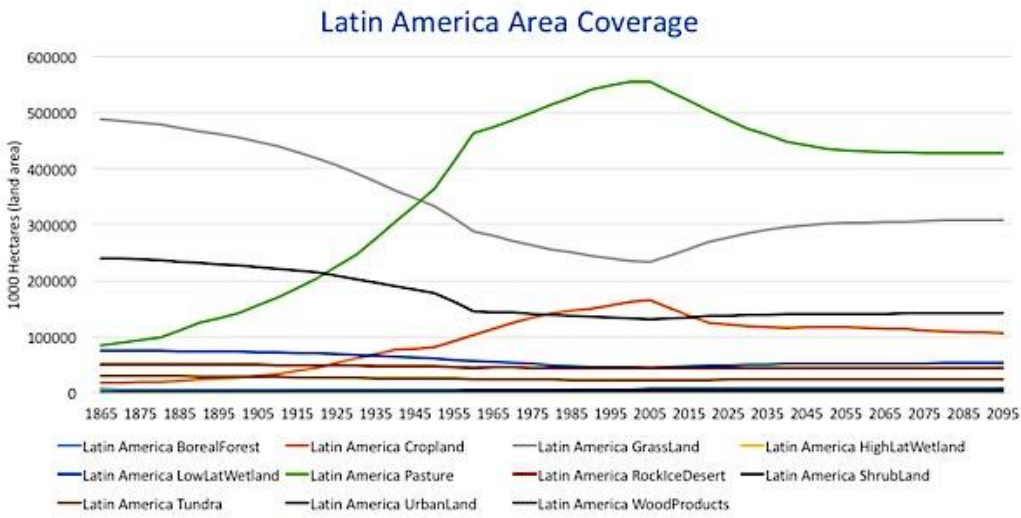


Figure 8.3. Latin America Area Coverage, Smith & Rothwell, 2013

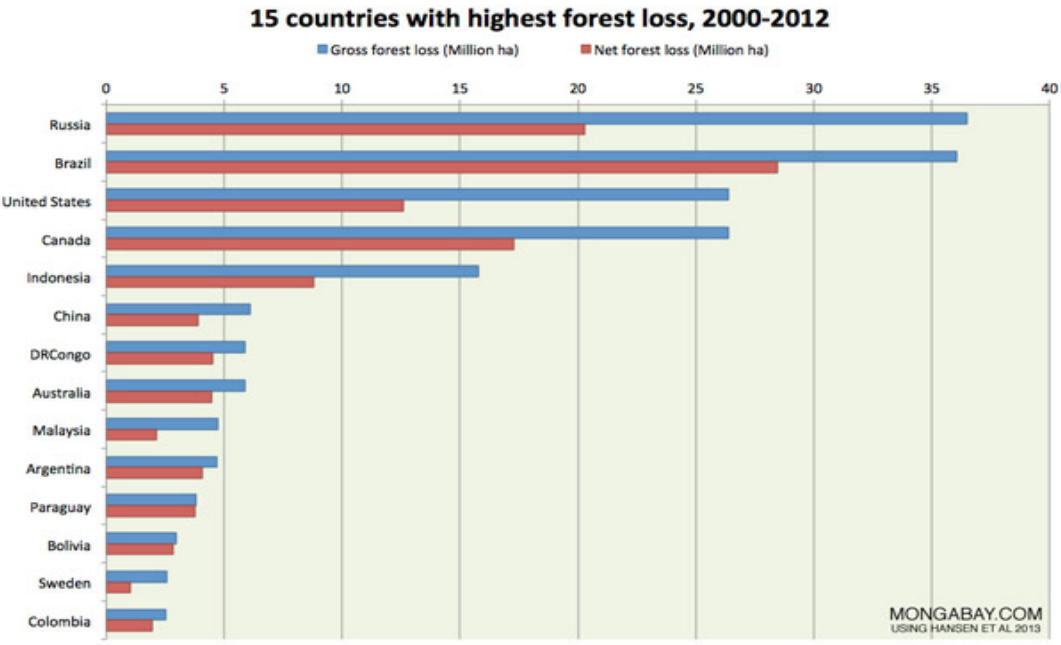


Figure 8.4. 15 countries with highest forest loss, Mongabay 2013

It has been established that converting natural ecosystems to crops results in SOC losses, and that the reversal, converting croplands to grasslands, forest lands or native ecosystems result in SOC gains. However, forests to grasslands did not have a change in SOC, but rather a decrease in the amount of above ground biomass. Thus, land use change can result in shifting a C sink to a C source. A specific example of this C loss was demonstrated using modelling and inventory results for land use change between 1990 and 2000 in the UK resulting in the land becoming a net source of CO₂, losing 6.5–9.4 million tonnes of C as CO₂ (with an uncertainty range of 50–100 percent) (Falloon et al., 2006; Smith et al., 2007a). Therefore, an effective implementation of land use policy and land management practices must be in place in order to protect existing C stocks, and it is imperative to properly manage and protect C stocks of high organic soils such as those found in the uplands, peatlands, grasslands and native forests.

8.2 *Stabilization of SOC by properly implementing management practices*

Stabilization SOC is necessary to maintain soil's function as a C sink rather than a C source. A sink is classified as any process, practice, or mechanism that removes CO₂ from the atmosphere. The climate, mineralogy, texture, type of vegetation, and land management practices all contribute to the potential of a soil to store carbon (McCarl, Metting & Rice, 2007). Although soil parent material and texture play a significant role, they cannot be changed; however, the land management practices are factors that can be controlled, resulting in an increase in residence time of SOC. Human impacts alter the terrestrial C pool by altering land use and land change. Intensifying land use can potentially reduce soil fertility (without additional inputs) and its ability to sustain high production, as well as soil resilience to extreme weather under climate change, pests and biological invasion, environmental pollutants and other pressures. Thus,

human disturbances of soil can be a major driving force of climate change. However, mitigation can be achieved by LULCFC practices that can remove atmospheric CO₂, that result in storing C within the terrestrial C pool. One approach to do this involves the implementation of soil C management practices that would enhance soil C sequestration. Examples of such management practices include, but are not limited to the following:

- Crop rotations
- Crop cover
- Inclusion of perennials
- Tillage management
- Land use change to grassland or forest
- Reduced grazing in grasslands
- Increase grassland productivity
- Species management
- Reduced use of lime and N fertilizers
- Reduce harvest residue removal
- Promote biodiversity
- Protection against disturbance.
- Carbon-nutrient stoichiometry to increase soil C sequestration
- Soil C sequestration resulting from biosolids application
- Organic Farming
- Afforestation
- Biochar Soil Amendment

In 2010 it was reported that emissions from Forrest and Land use accounted for 11% of total anthropogenic greenhouse gas emissions, which was 14% of total C emissions that year.

However, they concluded that these figures may be misleading and that they do not reflect the full potential of tropical forests to mitigate climate change (Goodman et al., 2014). This is because the forest and land use net flux is being composed on two major fluxes, deforestation emissions (2.6–2.8 Gt C/year) minus sequestration from forest regrowth (1.2–1.7 Gt C/year) (Goodman et al., 2014). They also reported that gross deforestation accounted for more than a quarter the total C emissions while tropical forests removed 22–26% of all anthropogenic C emissions in the 2000s (Goodman et al., 2014). This study also suggested that if deforestation

was stopped and regrowth was enhanced, that the tropical forests could possibly capture between 25–35% of all other anthropogenic C emissions (Goodman et al., 2014). However, with climate continuing to spiral out of control, forest could turn from sinks to net C sources. This makes forest related activities of great importance in both short- and long-term mitigation strategies because they seem to be the most economically feasible and cost-effective mitigation strategies that subsequently enhance the soil C storage. Therefore, immediate action is needed to utilize these natural mitigation solutions, in order to develop a coordinated and comprehensive forest-related mitigation policy as is it plays a major role in soil C stabilization (Goodman et al., 2014).

Croplands are needed to provide for the increase global populations and demand for food. Therefore, management practices must be in place to achieve maximum soil C stocks for a given soil used for agricultural. This can be achieved by implementing practices that increase the return of plant biomass C to the soil. Practices such as improved crop varieties, extending crop rotations, inclusion of perennial crops (Follett, 2001; West and Post, 2002; Lal, 2003; Freibauer et al., 2004), tillage and residue management to increase soil C retention and sequestration (Cerri et al., 2004), water management to maintain soil C stocks (Follett, 2001; Lal, 2004b), land use change to grassland or forest to increase soil C sequestration (Falloon et al., 2004; Ogle et al., 2003).

Reducing the graze intensity (Conant et al., 2005; Reeder et al., 2004), can promote increase in SOC stocks from grasslands, as well as increased grassland productivity (Conant et al., 2001; Soussana et al., 2004), species management for enhanced C storage (Fisher et al., 1994), reduced lime and N fertilizer additions, and managed return of farm waste to the soil.

The planting of native hardwood species, C conscious site preparation and harvesting (Johnson, 1992; Johnson and Curtis, 2001), longer rotation periods (Schulze et al., 1999), reduced N fertilizer use (Jandl et al., 2007), reduced liming (Brumme and Beese, 1992), protection against disturbance (Hirsch et al., 2001), reduced harvest residue removal (Richardson et al., 2002) can all positively influence forest lands C stocks.

The lack of scientific current scientific data and models that detect changes in SOC stocks is lacking. There is a need to share and combine current research on the many ecosystem interactions and changes in land use that result in changes in SOC stocks. The STEP-AWBH model proposed by Grunwald et al. (2011), is a spatio-temporal soil modeling framework, which accounts explicitly for anthropogenic forcings. This model can be applied to predict soil properties, including soil C, from a variety of environmental variables, and it is one step forward in tracking these changes over time to make predictions of potential shifts in SOC stocks with shifts in land use and change, Grunwald et al. (2011). The C fluxes between these soil C pools are spatially dynamic, and shift as a function of changes in the land-use, climate change, and other environmental or human-induced stressors (Cao, 2015), and the response of soil C dynamics from differences in these factors will affect both the future climate and the quality of ecosystems (Mathieu et al., 2015). Keeping track of the global C budget annually is crucial, for not only to tracking how much C is emitted to the atmosphere and the amount that stays there, and to see the changes in how much accumulates on land and in the ocean, but most importantly, because natural changes in the partitioning of emissions among these reservoirs (atmosphere, land, and ocean) may provide the first indication that the global C cycle is changing, perhaps in response to climatic change. The fact that C emissions into the atmosphere have doubled since the 1960's, yet there has not been a drastic increase in CO₂ because other C sinks have resulted

in doubling as well, demonstrating the resilience of earths system working together in balancing C in efforts to stabilize atmospheric CO₂, with the land and ocean sinks keeping the atmospheric increase at only half of what it would have been if all of the emissions had remained in the atmosphere. Nevertheless, there is a great need for advancing the scientific understanding the effects of land use and change on soil C storage to ensure that C measurements and models provide certainty in accounting for and predicting SOC stocks, that will lead to the development of a more meaningful land use policy for C sequestration in the 21st century.

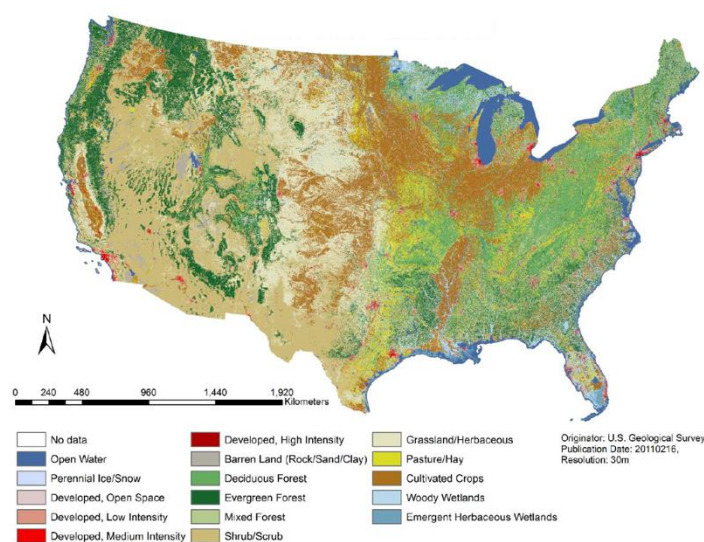


Figure 4-7. National Land Cover Dataset (NLCD) of 2006 for the contiguous U.S.

Figure 8.5. National Land Cover Dataset (Cao, 2015)

8.3 *Enhancing C sequestration in soil through the application of coal combustion products as a potential solution to increase SOC*

Coal accounts for approximately 40% of the total power generated from fossil fuels globally (IAEA 2012), contributing as much as 56 % of global greenhouse gas emissions (ASN Bank/Ecofys, 2013; Yunusa et al., 2014). However, during this process of harvesting the energy through the combustion of coal, 5-15% of the coal remains unburnt, left as solid residues called

Coal Combustion Products (CCPs) (Yunusa et al., 2014). One specific residue (>85%) is Coal Fly Ash (CFA), which are lightweight particles captured in exhaust gas by electrostatic precipitators and bag houses of coal-fired power plants (Dodge, 2014). According to the EPA, Coal ash is the largest type of waste generated in the United States and in many other countries, with over 100 million tons produced in the USA every year. The production of such a large quantity of waste has raised the question of its use and disposal to benefit plant productivity while sequestering C.

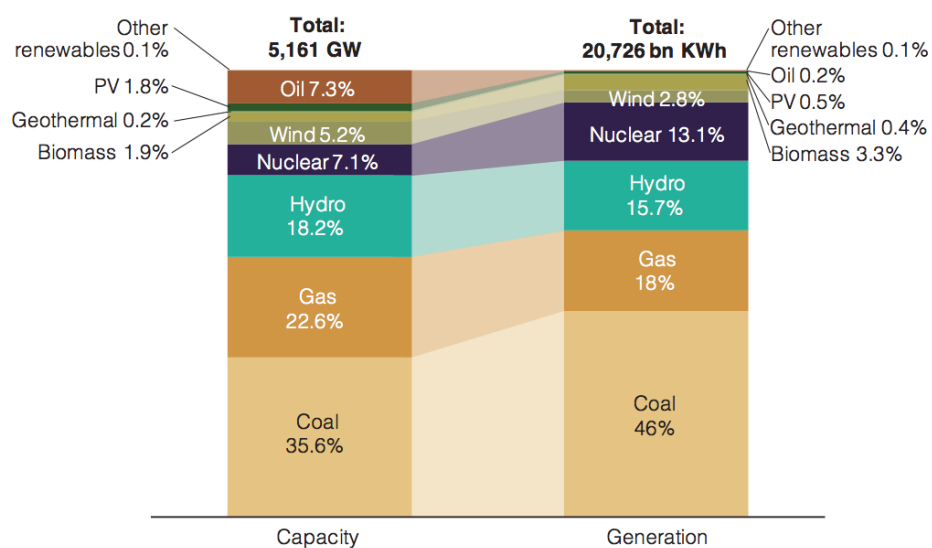


Figure 8.6. Global Net Electricity Capacity and Generation, World Energy, 2013.
https://www.worldenergy.org/wp-content/uploads/2013/09/WEC_J1143_CostofTECHNOLOGIES_021013_WEB_Final.pdf

In a recent study conducted by Yunusa et al., 2014, the use of coal combustion products for enhancing C sequestration in soil was investigated. In their study, they collected five Coal Fired Ashes (CFA) from power stations world-wide; three of which were alkaline, and 2 acidic. They were applied to soils that had been amended with and without manure. It was observed that both the acidic and alkaline CFA additions minimized the loss of C and N from acidic soil, with or without added manure, and that additions of CFA had no impact on the loss of C or N from unmanured soil that initially had low concentrations (Yunusa et al., 2014). On the other hand,

loss of C from manured soil was reduced by 36% with alkaline ashes and by 3-fold with acidic ashes; while loss of N was 30–50 % lower with acidic ashes, but 28 % higher with alkaline ashes, compared with no ash treatment (Yunusa et al., 2014). However, it was concluded that it was not the CFA that directly resulted in increases in soil C, but rather the indirect effect on the microbial community.

Based on these results, alkaline CFA can be used in place of the conventional lime to increase soil pH, ameliorating soil acidity, while reducing the emission of CO₂ produced from liming. The CFA rich in lime CaO (≥ 3.0 %) can directly adsorb CO₂ on to their particles through carbonation. Up to 7 % of CO₂ was absorbed through this process under natural conditions over a 20- year period, but the process is enhanced at high temperatures and pressure (60–90 °C; ~4.0 MPa) in the laboratory (Muriithi et al. 2013; Yunusa et al., 2014). When ash was used to increase pH in acidic soil, they found that it enhanced humification and reduced mineralization, stabilizing soil (Amonette et al. 2009; Yunusa et al., 2014). CFAs in acidic ashes contained high concentrations of oxides of P, Si, Ti and clay particles, while the oxides of cations in alkaline ashes, both of which contribute to the promotion of C storage and amelioration of acidity in soil. Soils amended with ash also improved the formation of aggregates (Yunusa et al. 2011) that can protect organic C from microbial decomposers (Beare et al 1994; Jastrow et al. 2007; Rabbi et al., 2013; Young and Ritz 2000; Yunusa et al., 2014).

CFAs ash particles called cenosphere, are a hollow spheres made largely of contain SiO₂ and Al₂O₃ and filled with air or inert gas, that can aid in adsorption capacity of the soil. The figure below shows the close-up view of individual cenospheres, revealing the macro-size (>10 µm) pores with fines spherical ash particles adhered onto the surface (Yunusa et al., 2014). The adsorption SOC to soil colloids makes it unavailable to soil microbes, thus it would be expected

that the addition of ash would aid in the adsorption of SOC. However, this is not the case. CFA has a low capacity for physical adsorption of organic C, with adsorption being only 7–10 mg C/g for Australian CFAs (Wang et al. 2008; Yunusa et al., 2014). Thus, the increase in SOC was due to the physicochemical properties of ash/soil mixtures when added to the soil, that indirectly resulted in a reduction microbial biomass, especially in manured soils (Yunusa et al., 2014).

Although, studies have shown that CFA can promote C sequestration, it may not be an environmentally feasible solution. According to the EPA, coal ash contains a toxic stew of chemicals including Pb, As, Hg and radioactive uranium. Therefore, further research is needed in improving this technology, with research focusing on the following: (1) characterization of the enzymatic processes in organic C mineralization in ash amended soil, (2) major forms of N loss from the system, (3) whether similar C sparing is possible with plant residues, and (4) optimum rates and mode of ash additions (Yunusa et al., 2014).

8.4 *Application and accelerating the weathering of Olivine to increase SOC*

(Schuiling & Tickell, 2014) suggested that artificially accelerating rock-weathering could lead to withdrawal of CO₂ from the atmosphere through mineral carbonation then chemically sequester CO₂ in the form of solid carbonates in a subsequent precipitation reaction. Olivine, Mg₂SiO₄ and Fe₂SiO₄, is formed through the crystallization of magma or by the alteration of dolomite by metamorphic recrystallization. The mineral's atomic structure allows for the substitution of Ca, Mn, or Ni in place of Mg and Fe, thus Olivine is easily altered by chemical weathering, slowly releasing essential plant nutrients into the soil profile. This process requires an aqueous solution for the initial mineral dissolution. Thus, the main drawback is the rate of the chemical reaction; however, grinding the mineral down to a powder can accelerate the

reaction rate, but low porosity and permeability within a soil can limit this transformation. Nevertheless, this method is low in cost when not considering the environmental costs and impacts of mining. It could also be used to ameliorate acidic soil in place of lime. Finally, the chemical products provide valuable nutrients, acid buffering ions of Mg and bicarbonate; iron, and silicic acid (Schuiling & Tickell, 2014).

Olivine Minerals	
Mineral	Chemical Composition
Forsterite	Mg_2SiO_4
Fayalite	Fe_2SiO_4
Monticellite	$CaMgSiO_4$
Kirschsteinite	$CaFeSiO_4$
Tephroite	Mn_2SiO_4

Table 8.2 Olivine Minerals

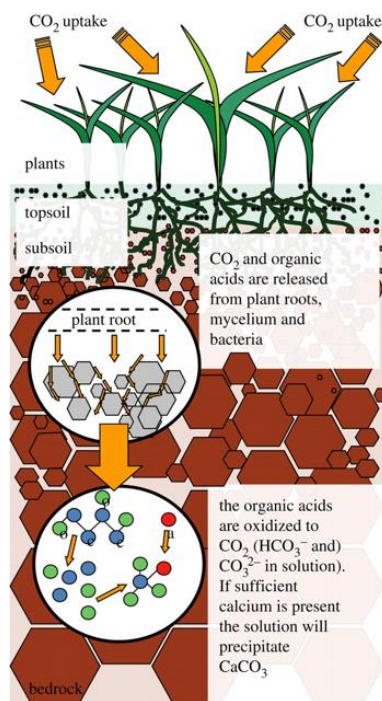


Figure 8.7 Capturing C through dissolution and precipitation. <http://plant-alchemy.blogspot.com/2011/07/capturing-carbon-in-soil-chelation-in.html>

8.5 *Application of Basalt powders as a potential solution to increase SOC*

Tropical soils tend to be low in fertility due to the rapid rate of weathering, decomposition, erosion, and leaching of nutrients under high temperatures and high annual precipitation in the tropics. The leaching of base ions results leads to extremely acidic soils that slow the growth rate of plants due to lack of nutrients (N, P, K) and minor essential soil nutrients (Mg, Ca, and trace essential metals such as Zn, Mn, Cu, and Mo). Not only do these soils have high acidity, but they tend to accumulate Al resulting in Al toxicity, further slowing plant growth. The leaching, high rate of organic matter decomposition under high mean annual temperatures, and erosional soil losses contribute to the typical low concentrations of tropical soil organic matter, and decreased retention of nutrients and water in the soil.

One method that has been proposed to combat this loss of SOC and nutrients is to promote plant growth by the application of basalt powders (Despaigne-Ceballos et al., 2014). Application of basalt powders can significantly enhance plant growth . The slow weathering of basalt releases essential nutrients required for plant growth. Although basalt powders do release nutrient element to soils, there is still a need to amend the soils with essential plants nutrients not present in basalt powders, such as N and C. However, the basalt powders aid in improving soil structure and retention of SOC. For a study in Panama, trees growing on basalt had noticeably more leaves and branches and darker-colored leaves (Despaigne-Ceballos et al., 2014). The basalt powder that was applied was enriched in P, K, Ca, Mg, Mn, Fe, and Zn, but its pH, organic matter, Cu, Al, or N content was not appreciably different from local soils (Despaigne-Ceballos et al., 2014). Trees often grow taller and leaves wider, capturing more C from the atmosphere to increase biomass production. Also, not only did plant growth increase, but the supplementation of basalt was cost effective, yet it is important to note that the benefits depended

upon local soil fertility and nutrient element deficiencies, the specific mineral needs of each plant, and climate (Despaigne-Ceballos et al., 2014). Although application of basalt powder enhanced plant growth in tropical soils of Panama, there is still a need to test this response on a wide range of plants, soils, rock powders, biochar, N, and climate regimes in order to ensure that its application will optimize the productivity and C storage benefits, as well as minimizing the cost for large-scale applications (Despaigne-Ceballos et al., 2014).

8.6 Application of biochar as a potential solution to increase SOC

Biochar is a fine-grained charcoal that has a high concentration of organic C and largely resistant to decomposition. Biochar is inexpensive, widely accepted, and offers many soil and microbial benefits. Biochar is produced by pyrolysis or gasification processes that heat plant biomass in the absence or shortage of oxygen (Yarrow, 2016). This residual charcoal by-product can occur naturally in agroecosystems due to incomplete combustion of plant roots or biomass, or as a by-product of the pyrolysis technology used for biofuel and bioenergy production (Yarrow, 2016).

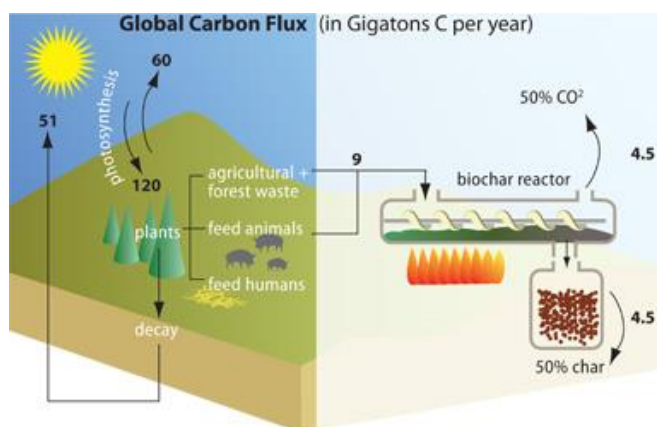


Figure 8.8 Biochar systems can reduce CO₂ and improve soil fertility, 2015 , <http://venearth.com/technologies/>

Biochar is not a nutrient, yet when applied to soils as an amendment, it can increase soil nutrient retention and reduce total fertilizer requirements. Biochar creates a recalcitrant soil C pool that is C negative—a net withdrawal of atmospheric C. Biochar has a high inner surface area estimated between a few thousand to maybe a million times more than external surface (Yarrow, 2016). This result occurs because the internal structure of biochar contains inner chambers or micropores, allowing for the adsorption of ions, water, and other molecules within a soil solution. The high surface area of the inner chambers and net negative charge of biochar result in high CEC, yet there is a weak attraction on the surface with ions in the soil solution, allowing access easy access of adsorbed nutrients to be released when needed or bioavailable (Yarrow, 2016). In fact, biochar has a greater adsorption capacity than clay mineral constituents, and the inner chambers provide a far greater ion adsorption capacity than almost all other natural materials. The exchange of ions with the soil solution and micropores allow nutrients of SOM to be in equilibrium with biochar, continuously recharging the soil solution with nutrients. Moisture is also retained, improving the water-holding capacity of the soil (Gurwick et al., 2013). The inner chambers act a nutrient reservoir and increase water holding capacity, preventing nutrients from leaching. The exchange of water and other chemical constituents between biochar and the soil solution enables more efficient nutrient flow between soil, root, and microbe (Wilson, 2014; Yarrow, 2016). However, based on a literature review report by Gurwik et al., 2013, some researchers have cautioned the use of biochar because it could have environmentally harmful adverse effects by releasing toxic substances such as heavy metals into soil or reducing the efficacy of pesticides (Gurwik et al., 2013).

Another benefit of biochar is its persistence in soil. The stability of biochar allows it to remain in soil for long periods of time, possibly for centuries, with a mean residence time

between 1300 and 4000 years (Wilson, 2014; Yarrow, 2016). This persistence is due to the slow nature of biochar degradation and weathering. Water does not dissolve biochar, nor do bacteria and fungi consume it at high rates. As cultivation of soil can decrease the soil C pool, the charcoal fraction is more resistant and thus its concentration tends to increase through time and may constitute up to 35% of the total permanent form of C in soil. Biochar has a half-life in soil over 1600 years (Yarrow, 2016).

The adsorptive ability of biochar has many advantages as it increases the retention of water and pollution. One advantage of the increased water-holding capacity and moisture retention of biochar-amended soils is that it can aid in preventing forest fires due to moisture retention. Also, biochar's ability to adsorb nitrates from soil solution prevents the leaching of nitrates into groundwater by 50%–80% (Yarrow, 2016). Additionally, biochar seems to alter microbial activity in soil, reducing soil respiration (CO_2) and conversion of N fertilizer to nitrous oxide (NO_x) that otherwise is emitted into the atmosphere. This is important because nitrous oxide is a GHG produced from microorganisms, with a warming impact over 300 times that of CO_2 , and it has been documented that biochar added to soils curtails outgassing of greenhouse gases by 37%–90% (Yarrow, 2016). Therefore, the ability of biochar to reduce leaching, outgassing methane and nitrous oxide and to improve the effectiveness of fertilizers make it advantageous for agricultural management.

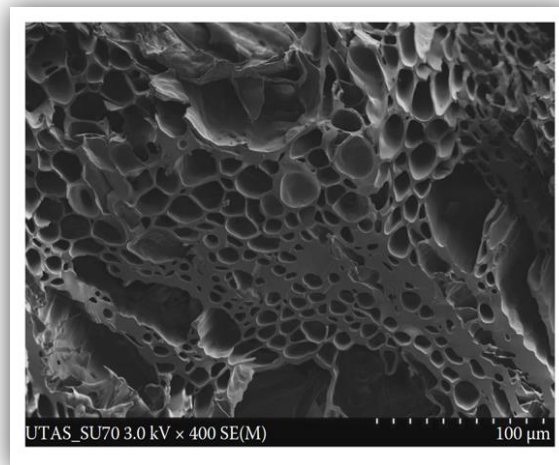


Figure 8.9. Red Cedar biochar scanning electron microphoto, UTAS_SU70 (Geotherapy 2015)

Biochar can also increase microbial activity as it offers a refuge for soil organisms by providing protection to survive, thrive, interact, and evolve at optimum density and diversity (Yarrow, 2016). The rate of mycorrhizae spore formation and germination has been reported to increase with biochar application, resulting in rapid growth. Increases of mycorrhizae fungi can improve the ability of plants to access soil water and minerals, even in dry conditions. Fungi use C from plants to assimilate glomalin as hairlike filaments, called hyphae. The fungi extend the hyphae into the soil, functioning as pipes to funnel water and nutrients, particularly P, to plants (Yarrow, 2016). Therefore, the enhanced growth results in dense mats of fungal hyphae that accumulate and when they die, their remains contribute a significant amount of OM to the SOM fraction. The produced glomalin glycoprotein has been reported as accounting for 27% of soil C, making it a major component of SOM (Yarrow, 2016). Then, the residual Glomalin binds with soil solid particles, promoting the formation of aggregates that enhance soil structure. In return, soil aggregates offer habitats that harbor beneficial microbes, hold more water, and resist soil surface encrustations.

A study of infertile Amazon clays reported that the initial biochar application can delay plant growth for 1 or 2 years, and then afterwards, plant growth improves and lower quantities of fertilizers are required. This is because biochar must first undergo a gradual transformation before it can sustain strong plant growth (Yarrow, 2016). The initial colonization of biochar and population explosion of soil microbes compete with plants, consuming much of the available nutrients soon after biochar application. Once microbial communities become established, they aid plants in gathering surplus nutrients directing it to roots for increased plant growth and productivity that can surpass the growth from the use of chemical fertilizers.

Nitrogen fixing *Rhizobium* bacteria also benefit from biochar applications. These bacteria produce a nitrogenase enzyme and transform N gas in the air to a form that is available for other soil organisms (Yarrow, 2016). These bacteria reside in the nodules of legume roots, converting N to a form that can be used and made available to plants. There are over 200 types of bacteria that convert N gas into a form that plants require for uptake, yet there is a need for more research to determine the microbes that prefer biochar as a host environment. Thus, enhancing the environment that promotes the growth of nitrate-producing microbes will reduce the dependence on the use of imported synthetic, fossil-fueled N. Christoph Steiner from the University of Georgia, reported that there was a 52% reduction of NH₃ loss when char is used as a composting accelerator (Yarrow, 2016). Therefore, biochar promotes microbial activity that results in increased SOC, yet there is a need for continued research in identifying the microbial strains that benefit from these applications, as well as their interactions within specific soils, crops, and climates.

The output of C from decomposing organic materials was reported to be between 50 to 60 billion tons (Gt) per year, while land use emits approximately 0.5 to 2.7 Gt C (Yarrow, 2016).

Even if small fractions of the soil C is sequestered as a result of biochar application, it could potentially make a significant global impact. It has also been hypothesized that the carbonization of agricultural and forestry wastes could capture 0.16 Gt C yr⁻¹, and if the demand for renewable fuels by the year 2100 was met through pyrolysis, biochar sequestration could exceed current emissions from fossil fuels (Yarrow, 2016). Additionally, the produced charcoal from forest fires could capture 50% of the above-ground C, yet a forest fire results in an above ground biomass, with only 2-3% of the above-ground C converted into charcoal. Nevertheless, slash and char, as well as the production of biochar as a byproduct renewable energy production in an ideal solution to significantly restore soil and sequester C.

For soil to truly be classified as stored or sequestered, it must be removed from the atmosphere for 100 years, and it has been found that biochar sequesters C 16 times longer than this minimum (Yarrow, 2016), which makes biochar C negative, or permanently removed from the atmosphere. Thus, soil can be regenerated with biochar applications, resulting in multiple positive feedback loops that accelerate C capture and sequestration. Not only is this technique simple, inexpensive, and widely accepted, but it could potentially store 2.2 Gt C (Yarrow, 2016). However, based on a literature review 2011 by authors Gurwick et al., 2013, of 311 peer-reviewed research articles published through, very few studies address the ecosystem processes influence by biochar applications (Gurwick et al., 2013). They also suggested that there needs to be further research to improve the understanding of factors such as the emissions associated with growing, harvesting and transporting feedstock; and with biochar production and application to soil. They concluded that there is insufficient data to draw conclusions about the effects of the whole-system GHG budgets from biochar production and applications, (Gurwick et al., 2013). Therefore, due to the sufficient research to support adoption of biochar systems, there is a need

to review the peer-reviewed literature covering the multiple benefits and risks biochar may deliver (Gurwick et al., 2013).

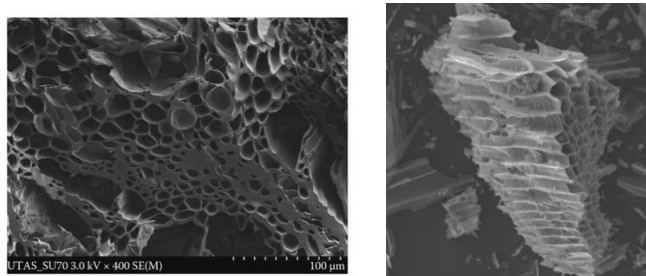


Figure 8.10. a. Biochar Scanning Electron Microscope (Yarrow, 2016); b. How biochar works in soil (Wilson, 2014).

Biochar Summary Evaluation Table

Biochar		
Effectiveness	Limited by plant productivity and conflicts over land use with agriculture and biofuels Burning biochar (in place of fossil fuels) may be preferable to burying it	Low
Affordability	Similar to biofuels (NB costs of fertilizers and transportation)	Low
Timeliness	Slow to reduce global temperatures (CDR method) Substantial prior research required to investigate efficacy and impacts	Low
Safety	Potential land-use conflicts (food vs. growth of biomass for fuel) Long-term effects on soils not yet known	Medium

Table 8.3. Biochar Summary Evolution Table, Shepard J.G., 2009. *Geoengineering the Climate: Science, Governance, and Uncertainty*.

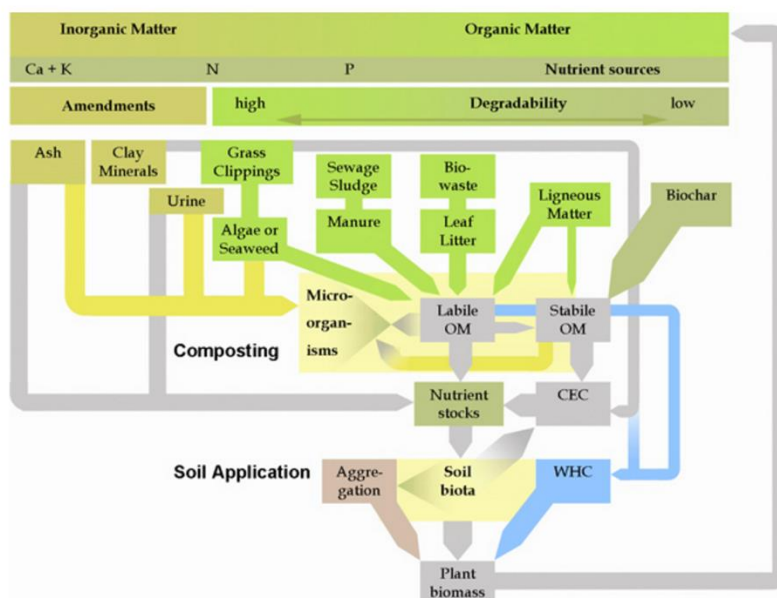


Figure 8.11. Sustainable management of natural resources combining biochar and inorganic wastes. <https://biochar-journal.org/en/ct/32>

8.7 Application of rock powders to enhance NPP as a potential solution to increase SOC

Application of rock powders as a form of fertilizer can promote the remineralization of denuded soils, making soils fertile, thus enhancing productivity. Soil remineralization (SR) creates fertile soils by returning the minerals to the soil (Campe et al., 2011). Rock powders act as fertilizers in mineral deficient soils, providing essential or limiting nutrients for infertile soils. The process involves the slow release of mineral constituents through chemical dissolution. Upon weathering, rock powders break down into finer soil constituents, improving the ion-exchange-capacity of soils, and plant nutrient availability. Minerals are slowly released making the affects long lasting.

Under proper remineralization protocols, this method has been found to increase growth primary productivity, and increasing NPP can result in increased soil C sequestration. Through many scientific studies, it has been observed that the addition of rock powders can increase

yields as much as two to eight times for agriculture and forestry (wood volume), and to have immediate results and long term effects with a single application (Campe et al., 2011). However, one drawback is the low rate of reaction from the limited surface area of the applied minerals, yet grinding the rocks down to increase surface area can alleviate this problem (Campe et al., 2011). Additionally, the effect of rock powders can be enhanced when amended with biochar, which aids in moisture and nutrient retention.

In a report by authors Campe et al., 2011, it was stated that through biological growth and sequestration of C as humus in the soil, the capacity to increase soil C levels 0.5% per year. It was also reported that basalt dust application at a rate of 150 tons per hectare to forest soils resulted in four times greater tree wood volume than controls after 24 years, and the benefits only tapered off after 60 years (Campe et al., 2011; Sauter & Foerst, 1987). A recent study in Panama compared tree growth rates over five years in highly infertile soils to those in basalt rock dust (Goreau et al., 2011). They found that the trees in basalt dust grew almost 10 times faster in terms of biomass (Campe et al., 2011). Additionally, the use of glacial moraine dust to Michigan soils resulted in higher yields of maize from 25 bushels/acre to 65 bushels/acre, as well as greatly increasing its nutritional value (Campe et al., 2011). According to the work of Alan Yeomans in Priority One (2005), it has been suggested that when rock salts are applied to infertile soils, the amount of C sequestered as a result from its application could potentially return atmospheric C to pre-industrial revolution levels in 5 years (Campe et al., 2011).

This simple, non-toxic, and inexpensive technique not only increases productivity, but offers a sustainable and superior alternative for pest management than insecticides and herbicides (Campe et al., 2011). The inert dust encourages the proliferation of resistant pests as the rock powders absorb or disrupt the waxy superficial layer of insects causing them to rapidly dry out.

Rock dust is capable of destroying and disabling insects to an extent that will limit their population and reduce crop damage. Rock dust act as an insect deterrent when sprayed on plant leaves, and the silica can strengthen plant tissue (which contain silica granules called phytoliths) and making them less susceptible to drought, insects, and diseases (Fragstein, 1995). However, it does not completely control insect life that would result in an ecological imbalance.

Other benefits include but are not limited to the following: rebalancing soil pH, increasing microbial and earthworm activity, increasing soil organic matter, preventing soil erosion, increasing the water storage capacity of the soil, increasing the resistance to insects, disease, frost, and drought and decreasing dependence on fertilizers, pesticides, and herbicides.

There is a growing body of scientific evidence showing that the addition of rock powders containing Ca, Mg, and Fe bearing silicate minerals increase growth and productivity of plants when applied to soils (Campe et al., 2011). Not only do crop yields increase, but rock powders offer disease and pest resistance through proper remineralization. Soils that have been degraded or depleted of base cations can be replenished through the slow release of rock powder minerals, restoring mineral deficient soils. This method is readily available depending on the local geologic materials and relatively inexpensive. Therefore, improving soil health and quality, and increasing plant productivity with additions of these mineral fertilizers, seems to be a simple, easy, practical means to promote soil C sequestration.

8.8 *The addition of organic amendments to as a potential solution to increase SOC*

The application of organic sewage wastes in the form of biosolids for agricultural offers a way to provide a source of OM and plant nutrients, increasing NPP and removal of atmospheric CO₂, ultimately completing the natural nutrient cycle (Torri et al., 2014). Biosolids

are typically composed of 40–70% organic matter, ranging from about 20–50% organic C content (Torri et al., 2014).

The application of biosolids could also promote an increase in SOM and C retention, improving soil fertility. Land application also offers an alternative for waste management; however, it should not be used as an alternative means of waste disposal for climate mitigation. Other benefits of using biosolids for land application include; decrease in bulk density, increase in pore size, soil aeration, root penetrability, soil water holding capacity, and biological activity, all of which may be reflected in an increase in crop yields (Torri et al., 2014)

Although biosolids may be advantageous for soil C storage, solution for waste, and providing plant nutrients, the use of biosolids has one major disadvantage; biosolids may contain constituents that can be harmful to humans and other organisms. Biosolids have been found to contain human pathogens and trace elements, including arsenic, Cd, Zn, Cu, Cr, Pb, Hg, Ni, and Se, all of which can pose human and environmental problems. Therefore, the current use of biosolids as a land application is limited.

After long- and short- term observations of biosolids applications, it has been found that soils amended with biosolids accumulate a significantly higher amount of organic C compared to mineral fertilized soils (Torri et al., 2014). When amending soils with biosolids, two fractions differing in degree of biodegradability exist; labile fraction (53–71%) which quickly decomposes at a constant rate, and the recalcitrant fraction (28.5–45.4%), resistant or unavailable to microbial organisms (Torri et al., 2014). Recalcitrant organic compounds of some biosolids comprised of stable cholestane-based sterols have a turnover rate in the order of hundreds of years. On the other hand, soils with a lower clay fraction tend to mineralize C at a faster rate. This is because the residual C can be protected by adsorption to clay particles or isolated from microbial

decomposition, which is due to limited access to SOC or lack of gas diffusion making the environment inhospitable for microorganisms. Although clay particles can offer physiochemical protection of SOC, there have been studies reporting that mineralization rates of biosolids-borne C were not related to soil texture, and in fact, the slow rate of turnover was due to other soil parameters, particularly pH. Soil pH was found to be a dominant variable on soil decomposition of biosolids (Torri et al., 2014). Low pH, or acidic soils, tend to delay decomposition of SOM resulting in an increase in the retention of biosolids-borne C, whereas soils higher in pH stimulated microbial activity, increasing C mineralization.

Biosolids containing amorphous Fe and Al oxides can also promote SOM stabilization (Torri et al., 2014). The surface area and charges create active surfaces that result in adsorption or complexation by Fe and Al cations with SOM. The strong association of SOM with secondary hydrous Fe and Al phases prevent degradation, as SOM access is inhibited or unavailable. Therefore, SOM could potentially be stabilized from long term applications of biosolids containing amorphous Fe/Al.

The application of biosolids, specifically containing sewage sludge, provides a source of labile C that is more easily decomposed, thus resulting in an increase of microbial activity (Torri et al., 2014). Initially, large amounts C-CO₂ are produced due to rapid decomposition and microbial growth. Whereas, compost or thermally dried sludge contains a higher portion of recalcitrant C, reducing rates of decomposition (Torri et al., 2014). There is an initial lag time for the adaptation of bacteria to begin to exploit new environmental conditions, especially in sludge containing high content of trace elements. Some authors reported that the strong microbial activity induced by the application of biosolids with high contents of labile organic substances would mineralize native SOC. However, the effects of biosolids applications is considered

controversial. Nevertheless, the long term, biosolids amended soils retain more C than soils under conventional agricultural regime in different tillage, fertilization, and rotational schemes (Torri et al., 2014).

Microbial proliferation and the increase of enzymatic activity can be enhanced through the interactions of the substrates or solids phase of biosolids. The presence of active enzymes reduces energy barrier to the decomposition of complex organic substrates thus facilitating the biosolids matrix mineralization without new and metabolically expensive synthesis of extracellular enzymes (Torri et al., 2014).

The organic matter within biosolids ranges from 40–70% that can be divided into two fractions based on the biodegradability; the labile or quickly mineralized fraction, and the recalcitrant fraction which is more the resistant fraction leading to SOC accumulation (Torri et al., 2014). The recalcitrant C fraction in biosolids is important when predicting the state or stabilization of C storage in soils. There is a direct relationship between the energy required for mineralization and the amount of recalcitrant in biosolids; the higher the C recalcitrance in biosolids, the higher the metabolic energy required for the mineralization of biosolids by soil microorganisms (Torri et al., 2014). Therefore, monitoring microbial and enzyme activity can give an indication of C stabilization.

As discussed before, soil texture and its physiochemical protection have a major influence on the stabilization of soil C; however, biosolid-borne C may not depend on soil texture, and that the soil pH may have a greater impact (Torri et al., 2014). Many studies reported that slightly acid soils retained more biosolids-borne C than soils with a higher pH. Also, biosolids contain amorphous Fe and Al- oxides play an important role in soil organic C accumulation. Therefore, because of the global heterogeneity of soils it is difficult to establish a

capacity of a soil to sequester biosolids-borne C. However, It has been well established from experiments in soils from different regions and under different management practices that application of biosolids to land increases C reserves of soils. Nevertheless, there are many benefits associated with the use of biosolids for soil C sequestration, as there is a need to investigate further in the long-term impacts on soil microbial communities due to the presence of contaminants that may be within biosolids.

Chapter 9. Conclusions

The future of climate is strongly dependent with the balance of soil C pool (Jones et al., 2003). Although there is a substantial amount of knowledge and understating of the soil C pool and its role in the global C cycle, many uncertainties remain that need to be addressed.

With global population on the rise, increasing the demands on the many ecosystem services that the soil provides, there is a need for improved data on global soil resources for sustainable development (Jandl et al., 2013)

Many studies have demonstrated mechanism to increase SOC, for example, by the addition of plant-derived C from external sources such as composts and biochar; however, there is insufficient data on the soil system as a whole, comprised of the many ecosystem interactions and processes, that integrate the many proposed solutions for sequestering C within the soil pool. Research gaps based on the uncertainty of the behavior of soil C need to be filled, as well as the use of different models that produce dramatically different predictions of future climate trends depending on the representation of ecosystem C (Friedlingstein et al., 2006). Therefore, our understanding of the functionality of the soil system is still limited (Cao, 2015), and there are

many research gaps related to the behavior of soil systems, such as the relationships between soil-forming factors and SOC (Cao, 2015).

Future studies also need to be focused on increasing the knowledge and understanding of the many spatial and temporal variations of SOC (Cao, 2015). The C fluxes between these soil C pools are spatially dynamic, and shift as a function of changes in the land-use, climate change, and other environmental or human-induced stressors, and the response of soil C dynamics from differences in these factors will affect both the future climate and the quality of ecosystems (Mathieu et al., 2015). Soil and ecological processes are interrelated related, and the wide scale spatial and temporal distributions have a great influence on these processes involved within the soil and global earth system. Increasing the current Understanding the dynamic system of soil to develop insight into biogeochemical processes and its interactions within and among earths systems would be advantageous for future predictions of SOC. Thus, there is a need to develop protocol and policy derived from an emergent of techniques to update our understanding soil data, involving the spatial behavior of soil and ecological variables. This requires that future research is needed to focus on the underlying ecological processes, as well as a full assessment of the many factors that may affect soil C observations and estimations of changes in SOC pool. Thus, it is of foremost importance to quantify the turnover times of C in terrestrial ecosystems and its spatial co-variability with climate.

Methods of sampling and quantifying SOC stocks needs to be improved. The variability of soil C with depth (>30 cm) needs to be better represented. There is a need for the development of a model that is used globally to accounts for the vertical distribution of SOC within a soil profile that can be used for large scale estimations. Models to estimate SOC must include the many processes and dynamics involved within a soil system representing the whole soil profile

(McBratney et al., 2015). Although there have been many studies reporting the dynamics of the surface layers of soil C, the subsoil C remains poorly understood and quantified (Trumbore & Czimczik, 2008; Rumpel & Kogel-Knabner, 2011; Harper & Tibbett, 2013). The current procedures used produce unreliable estimations of the total SOC pool, partly because the available knowledge based on previous studies have not clearly defined upper soil horizons, nor have they included the significant contribution of subsoil to SOC stocks. Therefore, the soil expert community needs to work together in creating standard protocols of soil surveying and lab procedures in order to produce reliable local, regional, and global SOC pool estimates. The use of long-term ecological research sites that have monitored and quantified the changes in SOC changes and the underlying mechanisms are investigated, need to be the foundation for a unified approach for a regional, national, and international SOC monitoring programs (Jandl et al., 2013).

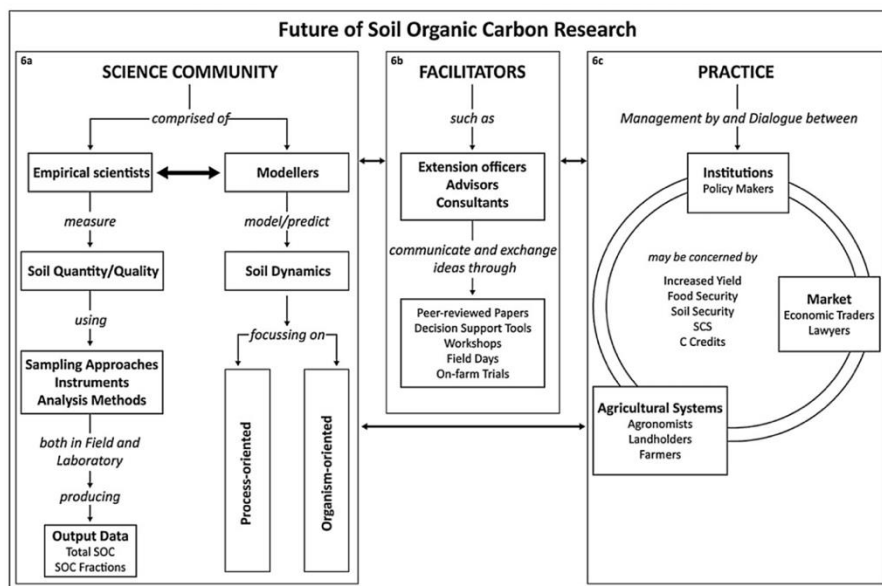


Fig. 6. Interdisciplinary research.

Figure 9.1

Research Gaps Reported Cao 2015 by Include:

- Sharing of up-to-date and relevant soil information among diverse sources remains challenging because of inconsistent use of soil classification, outdated observation sets, and imprecise methods.
- Soil C change at the continental scale in a world with a warmer climate, land use and socio-economic change is affected by environmental covariates and human forcings.
- Improve the accuracy and reduce the bias in existing coarse-scale soil C prediction models.
- Determining accurate baseline soil C stocks are important for projections of future climate change and modulations in the C cycle.
- Characterizing organic C (C) sinks and sources across large regions is critical to understanding the dynamics of soil C in the context of climate change.
- The comparison and synthesis of regional digital soil models is hampered by the fact that studies differ in terms of soil C measurement techniques, sampling densities, sample protocols, environmental covariates (predictor variables), and statistical and geostatistical methods used to predict soil properties.
- Identify the underlying ecological processes responsible for those patterns, which requires assessing factors that may affect soil C observations and the spatial behavior of soil and ecological variables.

Existing policies and practices that alleviate global change pressures on soils from land use and Management:

- Prevent conversion of natural ecosystems to other uses (e.g. protected areas, reduced deforestation, prevention of wetland drainage, intensification rather than extensification);
- Prevent soil degradation (erosion control, fire management, reduced tillage/conservation agriculture, long-term fallows, flood protection, use of organic amendments, intercropping, improved rotations).
- Soil/ecosystem restoration (e.g. peatland rewetting, afforestation, revegetation on degraded lands, improved grass varieties, appropriate animal stocking densities, bioremediation).

Policies to encourage such actions were recently reviewed by Bustamante et al. (2014) and include the following:

- Economic incentives, for example, special credit lines for low C agriculture and forestry practices and projects, payment for ecosystem services (such as C storage) and tradable credits such as C credits.
- Regulatory approaches, for example enforcement of environmental law to protect natural areas, set-aside policies
- Research, development and diffusion investments

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