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Overview of different aspects of climate change effects on soils

August 2014

NP Qafoku

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Richland, Washington 99352

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1.0 Introduction

Climate change that is defined by high atmospheric carbon dioxide (CO₂) concentrations (≥ 400 ppm); increasing air temperatures (2-4°C or greater); significant and/or abrupt changes in daily, seasonal, and inter-annual temperature; changes in the wet/dry cycles; intensive rainfall and/or heavy storms; extended periods of drought; extreme frost; and heat waves and increased fire frequency, is expected to significantly impact terrestrial systems, soil properties, surface water and stream-flow (Patterson et al. 2013); groundwater quality, water supplies and terrestrial hydrologic cycle (Pangle et al. 2014); and, as a consequence, food security and environmental quality. Increased global CO₂ emissions, estimated at 8.4 Pg carbon (C) yr⁻¹ in 2010, have accelerated from 1% yr⁻¹ during 1990–1999 to 2.5% yr⁻¹ during 2000–2009 (Friedlingstein et al. 2010), being the main driver of the global warming. Climate-change impacts, which already are being felt in agriculture, ecosystems, and forests, are expected to be diverse and complex.

The C cycle, the process by which C circulates between the atmosphere, oceans, and lithosphere, includes fossil fuel deposits and the biosphere of the earth (Falkowski et al. 2000). Terrestrial landscapes and ecosystems play a large role in the global C cycling. More than 75,000,000 Gt of C is present within the global C lithosphere pool; by far, the largest quantity of C, more than 60,000,000 Gt, is in the form of sedimentary carbonates, relative to the other C pools (i.e., 720 Gt in the atmosphere, 38,400 Gt in the oceans) (Falkowski et al. 2000). While much of the lithospheric inorganic C (IC) is currently considered to be unavailable to C cycling, abiotic processes associated with climate-induced soil acidification and accelerated mineral weathering could redistribute large quantities of C among the three major Earth's C pools (land, atmosphere and oceans) by significantly altering the C source/sink behavior of soils.

World soils, a large reservoir of reactive C, moderate the global C cycle and atmospheric chemistry (Lal 2013). The soil C pool includes the organic carbon (OC) (living organisms and organic compounds) and the IC (Prentice 2001; Rice 2002). About 2500 Gt C is stored in soils out of which 1550 Gt are OC and 950 Gt are IC (Lal 2004). Clearly, a substantial amount of C in soils is present in the form of carbonates, such as calcite (Lal 2008) and this IC pool may substantially contribute to the global C cycle under conditions of a changing climate.

The C cycle is dynamic and responsive to climate change (Lal 2013). The effects of non-uniform climate warming (Xia et al. 2014), and a variety of human activities have already altered the terrestrial chemical cycles and land-ocean flux of major elements, although the extent remains difficult to quantify (Hartmann et al. 2013). In addition, our current knowledge is insufficient to describe the interactions among the components of the earth system and the relationship between the C cycle and other biogeochemical and climatological processes (Falkowski et al. 2000; Tagliabue et al. 2014). Among uncertainties are fluxes in and out of soils and interfaces (emission and sequestration); the efficiency of natural soil sinks and factors controlling source behavior; mineral silicate, and carbonate weathering and carbonation; SOM protection, transformation and mineralization; the fate of eroded dissolved inorganic C (DIC) and dissolved organic C (DOC); and the stability of IC and OC sequestered in soils.

Climate change may also induce a suite of not well understood effects in soils all of which have the potential to affect and/or even control the C balance and elemental cycling in soils. Soil-related consequences include significant/dramatic changes in soils properties, surface water and groundwater quality, food (national) security, water supplies, human health, energy, agriculture, forests, and

ecosystems. However, the impact and consequences of climate-change variables on relevant reactions and processes occurring within the surface layer of the terrestrial systems (i.e., soil system) and those occurring at the soil-atmosphere and soil-subsoil interfaces currently are not well understood. In addition, extreme events caused by climate change (Angéilil et al. 2014) may have long-term effects on soils with poorly understood consequences.

Soil response to climate change is expected to be multifaceted and rather complicated because of 1) the presence of an intricate network of sequential, simultaneous and/or coupled (often, time-dependent) chemical, biological and hydrological reactions and processes; 2) chemical elements, nutrients, and contaminants involved in these reactions and processes are distributed in the soil solid, liquid, and gas phases; 3) the scale-dependent effects related to mineralogical, chemical, and physical heterogeneities; and 4) climate extremes (e.g., heat waves and dry spells) induce interconnected short- and long-lasting effects in soils that currently are not well understood. To address these and other related issues mentioned above, studies should be conducted at different spatial scales [molecular, nano, soil particle (μm), soil aggregate (mm), soil horizon (cm), soil type, soil order, regional, and global] and temporal scales (minutes to day, days to year, years to decade, decades to century, centuries to millennium, and millennia to epoch/era).

The objective of this review is to initiate and further stimulate discussion about climate-change effects on soils; present the state-of-the-science in important topics related to C and elemental cycling and SOM role in fate; and provide ideas for future research directions and needs based on research results and recommendations derived from recently published articles mainly in high visibility journals. In this report, the discussion will be focused mainly on important and challenging aspects of climate-change effects on soils, such as climate-induced accelerated weathering of soil minerals; SOM protection, transformation and mineralization; SOM temperature sensitivity; and C and elemental cycling in soils. This review reports recent discoveries and identifies key research needs required to understand the effects of climate change on soils.

2.0 Climate-Change Induced Accelerated Soil-Mineral Weathering and C Cycling

2.1 Accelerated Mineral Weathering

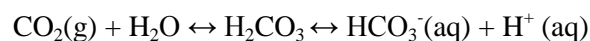
Interest in soil-mineral weathering has increased over recent years because of the possible effects of climate change on soil properties and environmental quality and food security; the role soils play in controlling global C cycle; and the positive or negative feedback to a warming climate. The weathering of alkaline rocks, such as alkaline or alkaline earth silicates, is thought to have played an important role in the historical reduction of the atmospheric CO₂ (Kojima et al. 1997), and will have an important role in the evolution of the global C cycle over the next century (Beaulieu et al. 2012), when climate change is expected to be significant.

Accelerated weathering of the rocks and minerals in soils will be promoted by higher atmospheric CO₂ concentrations (≥400 ppm) and temperature (which increase the extent and rates of weathering), intensive rainfall (which facilitates the removal of reaction products either by surface runoff or percolating water), and heat waves and extended periods of drought (which promote physical alteration of rocks and minerals). The results from a 44-year field study show that weathering rates are already increasing because of global warming (Gislason et al. 2009). However, the spatial patterns, temporal trends, and controlling factors of the processes and reactions and their effects on different scales, especially regional, continental, and global scales, are not fully understood at this time (Moosdorf et al. 2011).

In addition, although the effects of weathering, intensive leaching and soil acidification have been studied in the past [e.g., studies conducted with highly weathered tropical and subtropical soils (Qafoku et al. 2004; Qafoku et al. 2000; Bellini et al. 1996; Fiantis et al. 2009)], many positive and negative effects of climate-change induced accelerated weathering are not well studied and understood. On the positive side, weathering has the potential to increase the IC pool in soils via carbonate mineral formation, thus contributing to decreasing atmospheric CO₂ concentration. In addition, dissolution promoted release of elements that serve as nutrients for microbes and plants may stimulate microbial activity and increase plant productivity and biotic C sequestration, which will further increase C removal from the atmosphere. On the negative side, the acceleration of weathering may perturb the balance of processes not only in the biotic C cycle but also in the abiotic C cycles within soils, thereby controlling and/or affecting the distribution of C into less stable soil pools; increasing contaminant mobilization that may significantly alter soil microbial activity, plant productivity, life in soils, and C and elemental cycling; and possibly changing in a significant way the elemental balances in rivers, lakes, and oceans.

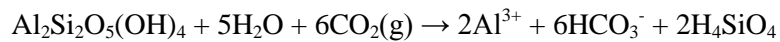
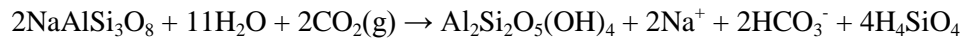
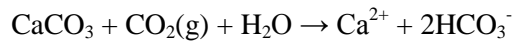
2.1.1 Soil Acidification and Weathering

The dissolution of atmospheric CO₂ gas in soil water and the subsequent formation of carbonic acid followed by its dissociation cause a decrease in soil pore water pH as a result of aqueous phase proton enrichment through the following chemical reaction:



Experimental and modeling studies conducted with soil and subsoil materials have shown a decrease in aqueous pH of 1 to 3 units in soil pore water as a result of excess exposure to CO₂ gas (Altevogt and Jaffe 2005; Little and Jackson 2010; Lu et al. 2010; Vong et al. 2011; Wang and Jaffe 2004; Wei et al. 2011; Wilkin and DiGiulio 2010; Zheng et al. 2009; Kharaka et al. 2010). A decrease in pH on the lower end of this range is typical of well-buffered systems in which CO₂-induced dissolution of reactive carbonates, silicates, and clay minerals provides enough buffering capacity (via HCO₃⁻ alkalinity) to resist changes in pH. Poorly buffered systems (e.g., sandy soils) have low abundance or are devoid of alkalinity-producing minerals and, therefore, lack the ability to resist changes in pH. In such systems, the decrease in pH is generally more pronounced and may have long-term consequences, and the risk for pH-induced perturbation of these systems is more significant compared to well-buffered systems (McGrail et al. 2006; Wilkin and DiGiulio 2010; Wang and Jaffe 2004).

The following reactions describe the dissolution of soil minerals such as calcite, feldspar and a typical 1:1 phyllosilicate in the presence of an excess amount of CO₂ gas [(Harvey et al., 2013) and the references cited therein]:



The dissolution rate of a rock or mineral is likely to be a function of its composition, crystallinity, composition and temperature of the aqueous phase (Gislason et al. 2010), the external surface roughness and internal porosity (reactive surface area), occurrence as single particles or in aggregates, and location within aggregate structure. Among the most important soil-related controls on the extent and rate of dissolution are soil mineralogy (i.e., minerals that are more or less resistant to weathering), soil type (i.e., highly weathered or less weathered soils), calcite content (i.e., soils with appreciable amounts of calcite with higher buffering capacity to resist changes in pH or soil with less or no calcite), soil texture (i.e., sandy or clay soils) and internal and external reactive surface area. It follows, therefore, that a broad array of soil responses to changes in climate related variables is quite possible.

2.1.2 Accelerated Weathering (The Case of Mine-Tailings and Mountain Denudation)

Publications on accelerated weathering of soils induced by climate change are not present in the current literature. However, papers covering the related topic of the impact of climate change on mine-tailings weathering and, more recently, mountain weathering and erosion have been published recently. Weathering of mine-tailings is expected to proceed more rapidly under global warming because of the dual effects of climate-change variables on weathering and increased acidity generated during weathering, which further accelerates mineral weathering (Wilson et al. 2006; Wilson et al. 2009; Wilson et al. 2010; Mills et al. 2010; Wilson et al. 2011; Bea et al. 2012; Tripathi et al. 2014). A positive effect of mine-tailings weathering is atmospheric CO₂ sequestration via carbonation of mine-tailings (an in-depth discussion about this topic is included in another section of this report). On the other hand, more rapid weathering of mine-tailings may increase contaminant mobilization, and this aspect of mine-tailings weathering seems to be overlooked in the current literature.

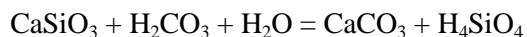
An important aspect of climate-change induced weathering in mountainous terrestrial systems is the relationship between weathering and erosion. It is widely recognized that these processes are positively correlated across diverse landscapes, although there are limits to this relationship that remain largely untested (Dixon and von Blanckenburg 2012). Using new global data compilations of soil production and weathering rates from cosmogenic nuclides and silicate weathering fluxes from global rivers, Dixon and von Blanckenburg (2012) showed that the weathering-erosion relationship was capped by what they called “speed limits.” Their estimates indicated a soil production speed limit of between 320 to 450 t km⁻² yr⁻¹ and an associated weathering rate speed limit of roughly 150 t km⁻² yr⁻¹. According to the authors, these limits are valid for a range of lithologies and also extend to mountain belts, where soil cover is not continuous and erosion rates outpace soil production rates. The influence of climate on the formation rates of regolith (i.e., the mantle of physically, chemically, and biologically altered material overlying bedrock), which covers much of earth’s continents, was investigated in another recent paper (Dere et al. 2013). Studies and research efforts similar to the latter study should be further expanded to better understand future effects of climate-change variables on soil weathering.

2.2 Weathering-Induced C Fluxes

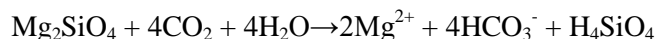
2.2.1 Atmospheric C Consumption During Mineral Weathering and CO₂ Breathing

Atmospheric CO₂ consumption by chemical weathering is the transformation of CO₂ gas into dissolved bicarbonate ion whose negative charge is balanced by cations such as Ca, Mg, Sr, Fe, and Mn released from chemical weathering of carbonate and silicate minerals (Renforth 2012; Cao et al. 2012; Kelemen and Matter 2008; Tomkinson et al. 2013; Kelemen et al. 2011; Thom et al. 2013; Ryskov et al. 2008). The uptake of atmospheric/soil CO₂ by carbonate rock dissolution plays an important role in the global C cycle, as it is one of the most important C sinks (Cao et al. 2012).

It is well stated in the literature that most C on earth is bound within minerals (Wilson, Raudsepp and Dipple 2006), and atmospheric CO₂ consumption as a result of weathering is an important and integral part of the global C cycle (Moosdorf et al. 2011; Li et al. 2014). Soil minerals, such as wollastonite, which is an alkaline silicate mineral, can provide the divalent cation needed to capture atmospheric CO₂ at ambient environmental conditions via the following reaction (Salek et al. 2013):



Olivine dissolution is accompanied by the sequestration of 4 moles of CO₂ for each mole of olivine through the following reaction (Köhler et al. 2010):



Chemical weathering of continental surfaces consumes 0.3 Gt yr⁻¹ of atmospheric C (Gaillardet et al. 1999). This flux is of the same general magnitude as the net uptake of CO₂ by the terrestrial biosphere (0.4 Gt C yr⁻¹) in pre-industrial conditions (IPCC Climate Change 2007). Other studies have shown that about 64% of the average bicarbonate flux caused by chemical weathering in North America originates from atmospheric CO₂ and 36% from dissolution of carbonate minerals (Moosdorf et al. 2011). However, the spatial patterns of dissolution and consumption of atmospheric C and the controlling factors at

different scales are not well understood. There is a need for a globally representative set of regionally calibrated models of CO₂ consumption by chemical weathering and its subsequent fate, which would apply very detailed spatial data to resolve the heterogeneity of processes occurring at the earth surface (Moosdorf et al. 2011).

A recent study has shown that global IC interactions and feedbacks in the lithospheric and atmospheric interfaces may be even more dynamic than previously thought. Carbonate anions intercalated within layered double hydroxides, a class of hydrotalcite, may undergo an unusual dynamic exchange with carbonate anions derived from atmospheric CO₂ under ambient conditions (Ishihara et al. 2013). The authors show that the rate of exchange is promoted by low relative humidity levels because of the formation of interlayer nanospace vacancies that acted as initial points for CO₂ uptake from air. Because various hydrotalcite-like minerals exist in soils, it is important to determine the extent and rates of the “soil mineral CO₂ breathing” and subsequent “weathering” of structural carbonate under changing climate conditions, especially in response to wet/drying cycles and increasing CO₂ concentrations in the atmosphere.

2.2.2 Inorganic C and Carbonation

Carbonation is the water-mediated replacement of silicate minerals by carbonate minerals in the Earth’s (or even Mars’s) crust (Kojima et al. 1997; Olsson et al. 2012; Thom et al. 2013; Tomkinson et al. 2013). Carbonation is important in understanding earth’s C cycle and mineral weathering (Kelemen and Matter 2008; Kelemen et al. 2011). Soils contain both carbonate remnants from the rocks (i.e., lithogenic carbonates) and pedogenic carbonates formed during soil formation (Ryskov et al. 2008). Apparently, the abundance of pedogenic carbonates depends primarily on the climate condition and, to a lesser extent, on soil age and content of lithogenic clasts in the parent material (Ryskov et al. 2008). These researchers found two epochs of carbonate formation in the soils of European Russia that coincide with periods of arid climate occurring approximately 3750 and 2300 years ago.

Minerals within the soil environment can capture and store atmospheric C through a two-step process: soil-mineral weathering followed by secondary carbonate mineral precipitation (Washbourne et al. 2012). This process provides a unique and efficient mechanism for CO₂ sequestration in surface terrestrial environments. The dissolved CO₂ (and aqueous bicarbonate) in the soil liquid phase is combined with other reactants released during soil-mineral weathering. The increasing activity of weathering reaction products, such as Ca, Mg or Fe, and HCO₃⁻, could lead to supersaturation of the soil solution and precipitation of carbonates [e.g., calcite (CaCO₃), magnesite (MgCO₃), and siderite (FeCO₃)]. This is a naturally occurring C sequestration pathway that could contribute to the global-scale efforts to reduce C concentrations in the atmosphere. Studies have shown that, in the course of soil formation over the last 5000 years, the soil fixed atmospheric CO₂ as pedogenic carbonate during arid periods at a rate of 2.2 kg C m⁻² y⁻¹ in chernozem (Typic Calciustoll), 1.13 kg C m⁻² y⁻¹ in dark-chestnut soil (Typic Haplocalcid), and 0.86 kg C m⁻² y⁻¹ in light-chestnut soil (Typic Natrargid) (Ryskov et al. 2008).

The rate of dissolution of silicate minerals is usually the limiting step in the two-step process of soil-mineral dissolution and CO₂ trapping in the newly formed pedogenic carbonate phases (Gislason et al. 2010). The temperature and composition of the contacting solution also would affect the extent and rate of dissolution and precipitation, and it is expected that the response would be dependent on the parent rock type. For example, the higher divalent metal content of ultramafic and mafic rocks would make them

better candidates for carbonation than sandstone. Previous research suggests that such compositional variations can result in about two orders-of-magnitude difference in the rate of carbonation (Gislason et al. 2010).

Several studies have demonstrated mineralogical trapping of CO₂ via mineral carbonation under conditions associated with deep geologic CO₂ storage (Loring et al. 2011; Oldenburg and Unger 2003; Bearat et al. 2006; McGrail et al. 2009; Harvey et al. 2013; Birkholzer et al. 2008; Langmuir 1997), but similar assessments have not been considered for climate-change induced mineralogical trapping of atmospheric CO₂ in surface environments (soils included). A full discussion of thermodynamic and kinetic limitations to pedogenic carbonate precipitation in subsoil environments is provided in the review paper by Harvey et al. (2003). While calcite may be readily formed in most soil environments, there are important kinetic limitations to precipitation of some other carbonate minerals (e.g., magnesite, dolomite, and siderite) even in cases where soil solutions are supersaturated with respect to these phases (Saldi et al. 2009; Arvidson and Mackenzie 1999; Jimenez-Lopez and Romanek 2004). This might be explained by the differences in surface charge density between Fe²⁺ and Ca²⁺ or Mg²⁺ and Ca²⁺ ions and the higher activation energy required to initiate dehydration of dissolved Fe²⁺ and Mg²⁺ ions and precipitation of siderite, magnesite, or dolomite. However, precursors such as nesquehonite (MgCO₃·3H₂O) may form in low-temperature CO₂-rich solutions that are supersaturated with respect to magnesite (Loring et al. 2012; Harrison et al. 2013; Beinlich and Austrheim 2012). Atmospheric CO₂ consumption may therefore occur via formation of these precursors in soils, although additional work is needed to study the stability of these phases under different soil and climate-change conditions.

Some authors have noticed that calcite precipitation can be inhibited by natural SOM dissolved in solutions (Lin et al. 2005). SOM may sorb to the calcite surface, and the greatest degree of inhibition has been observed for the highest molecular weight and aromatic C content of the materials (Lin et al. 2005). However, the degree to which the SOM/calcite interactions control calcite precipitation under different conditions and are affected by climate-change variables is unknown.

Microbes may play an important role in carbonate formation (Kenward et al. 2009; Power et al. 2011; Roberts et al. 2004). Examples include the formation of dolomite in a basalt aquifer on time-scales of weeks to months mediated by methanogens (Roberts et al. 2004). The rate of carbonation may be increased by carbonate-forming microorganisms that use their cells as a seeding/nucleation surface (Dong 2010; Douglas and Beveridge 1998). The presence of a suitable seeding surface can increase carbonate precipitation rates by up to threefold (Lin and Singer 2005). Microbe-mediated carbonate formation (Mozley and Burns 1993) and generation of bicarbonate ions used in hydrophyte photosynthesis, both processes resulting in IC (i.e., the HCO₃⁻ ions) being converted to OC (Cao et al. 2012), are other pathways of atmospheric CO₂ removal and transformation in soils that may be important under changing climate conditions. Clearly, elucidating microbially mediated feedbacks is fundamental to understanding ecosystem responses to climate warming, and would help provide a mechanistic basis for C-climate modeling (Zhou et al. 2012).

One last important topic in this section is the possibility of secondary phase formation, other than carbonates, resulting from accelerated soil weathering. Experiments conducted to study olivine weathering demonstrated the formation of goethite, hematite, silica, and carbonate minerals both in the presence or absence of air; formation of Fe³⁺ oxides in the absence of oxygen suggested hydrolysis, where water was converted to hydrogen and oxygen (Olsson et al. 2012). The formation of other secondary

phases, in addition to carbonates, is a very important aspect of soil response to climate change that needs attention and further exploration.

2.2.3 Carbonation of Mine-Tailings and Urban Soils

Many recent studies have addressed the topic of CO₂ sequestration via weathering and carbonation of mine-tailings (Wilson, Raudsepp and Dipple 2006; Wilson et al. 2009; Wilson et al. 2010; Wilson et al. 2011; Bea et al. 2012; Mills et al. 2010; Tripathi, Singh and Nathanail 2014). Characterized samples of neophases present in mine-tailings indicated that modern atmospheric CO₂ was used during mineral formation in a soil-like environment with characteristics similar to soil carbonate (Wilson et al. 2009). Carbonate phases include hydrated Mg carbonate minerals such as nesquehonite [MgCO₃×3H₂O], dypingite [Mg₅(CO₃)₄(OH)₂×5H₂O], hydromagnesite [Mg₅(CO₃)₄(OH)₂×4H₂O], and less common lansfordite [MgCO₃×5H₂O]. The potential for decomposition of metastable hydrated Mg carbonate phases to geologically stable magnesite represents a possible pathway of long-term mineral CO₂ sequestration in mine-tailings (Wilson, Raudsepp and Dipple 2006). Dypingite also may precipitate out of high-pH, high-salinity solutions (Wilson et al. 2010).

Other studies have found that atmospheric CO₂ is naturally sequestered in ultramafic mine-tailings as a result of the weathering of serpentine minerals [Mg₃Si₂O₅(OH)₄] and brucite [Mg(OH)₂], and subsequent mineralization of CO₂ in hydrated magnesium carbonate minerals, such as hydromagnesite [Mg₅(CO₃)₄(OH)₂×4H₂O] (Bea et al. 2012). In this study, kinetic dissolution of serpentine, dissolution-precipitation of brucite and primary carbonates-calcite (CaCO₃), dolomite [MgCa(CO₃)₂], magnesite (MgCO₃), as well as the formation of hydromagnesite, halite (NaCl), gypsum (CaSO₄×2H₂O), blödite [Na₂Mg(SO₄)₂×4H₂O], and epsomite [MgSO₄×7H₂O], were considered.

The rate of CO₂ sequestration via carbonation also is reported in a few recent studies. For example, silicate weathering trapped 102-114 g C m⁻² y⁻¹ within the nesquehonite structure, which corresponded to a two orders-of-magnitude increase over the background rate of CO₂ uptake predicted from arctic and subarctic river catchment data (Wilson et al. 2011). The predicted rate for CO₂ sequestered in ultramafic mine-tailings ranged between 600 and 1000 g C m⁻² y⁻¹, with the rate being sensitive to CO₂ diffusion through the mineral waste (Bea et al. 2012). The rate of CO₂ diffusion into different soils and under different conditions imposed by climate change is not known. Another study focused on re-vegetated mine spoils over a 19-year period in India. These mine spoils acted as source of pollutants with respect to air dust and heavy metal contamination to soil and water (Tripathi, Singh and Nathanail 2014). However, they also can act as a significant sink for atmospheric CO₂ through combined plant succession and soil formation (an accumulation of total C in total plant biomass, mine soil, and soil microbial biomass of 44.5, 22.9, and 1.8 t ha⁻¹, respectively) (Tripathi, Singh and Nathanail 2014). Total sequestered C increased by 712% after 19 years (a sequestration rate of 364 g C m⁻² y⁻¹).

There are two additional issues that are important in this discussion. The first issue is related to the necessity to determine the rate-limiting step in a sequence of steps that lead to carbonate formation. Studies have reported that dissolved IC concentrations decreased during dypingite precipitation, indicating that the rate of CO₂ uptake into solution was outpaced by the rate of C fixation via precipitation and implying that the CO₂ gas uptake is the rate-limiting step to CO₂ fixation (Wilson et al. 2010), although other variables should be considered as well. Further studies to elucidate this important aspect of mineral carbonation are required.

The second issue has to do with the possibility of formation of other phases (e.g., sulfates) during tailings weathering, in addition and/or in competition with the carbonates. For example, the relatively unstable Na-Mg hydrated double salt konyaite [$\text{Mg}(\text{SO}_4)_2 \times 5\text{H}_2\text{O}$] may be formed in tailings at the Mount Keith mine in Western Australia (Mills et al. 2010). These authors found that Mg bound to sulfate mineral phases reduced the overall potential of mine-tailings to sequester atmospheric C in Mg carbonates, such as hydromagnesite. In addition, amorphous sulfates that formed during konyaite transformation were highly reactive and may contribute to acid mine drainage if present in sufficiently large quantities, and may dissolve carbonate phases that have already sequestered C (Mills et al. 2010), releasing it back to solution and/or atmosphere. The regional and global effects of these processes are currently unknown.

Another recent study illustrated the potential for managing urban soils as tools of C capture and storage, and demonstrated the importance of studying C storage in engineering urban anthropogenic soils (Washbourne, Renforth and Manning 2012). According to the authors, the potential for using engineered urban soils to capture and store atmospheric C was high. In this study, anthropogenic soils, which contained substantial quantities of minerals that are rich in Ca and Mg ($21.8 \pm 4.7\%$ wt CaCO_3) derived from demolition activity (particularly cement and concrete), were systematically sampled. Isotopic analysis suggested that up to $39.4 \pm 8.8\%$ of the carbonate C has been captured from the atmosphere through hydroxylation of dissolved CO_2 in high-pH solutions, while the remaining carbonate C was derived from lithogenic sources. The CO_2 removal rate was $12.5 \text{ kg CO}_2 \text{ Mg}^{-1} \text{ y}^{-1}$ (Washbourne, Renforth and Manning 2012).

2.2.4 Inorganic C Flux Out of Soil: Transport to Subsoil/Groundwater, Rivers, Lakes, Oceans

Another important aspect of soil weathering is related to the fate of the weathering reaction products (such as dissolved IC and aqueous species of different chemical elements), which will either precipitate and undergo other in situ processes in soils (such as adsorption or uptake by ecosystems), or be transported via surface and groundwater to rivers, lakes, and oceans (Cao et al. 2012). A substantial amount of the atmospheric C taken up on land through photosynthesis and chemical weathering is transported laterally along the aquatic continuum from upland terrestrial ecosystems to the ocean (Regnier et al. 2013). Rivers transport the soluble products of weathering [e.g., cations, alkalinity, silicic acid (H_4SiO_4), etc.] to the oceans, where they are used by marine ecosystems (Street-Perrott and Barker 2008). Data on river-water quality from 42 monitoring stations in the Lower Mekong Basin obtained during the period 1972–1996 was used to relate solute fluxes with controlling factors such as chemical weathering processes (Li, Lu and Bush 2014). Calcium and bicarbonate dominated the annual ionic composition, accounting for ~70% of the solute load (Li, Lu and Bush 2014). In oceans, biological C pumps (which export OM and CaCO_3 to the deep ocean) may be altered by the resulting influx of elements and alkalinity (Hartmann et al. 2013).

Anthropogenic perturbation may have increased the flux of C to inland waters by as much as 1.0 Pg C y^{-1} since pre-industrial times, mainly resulting from enhanced C export from soils (Regnier et al. 2013). However, although it may appear that this process has potential to significantly increase ocean alkalinity, which can partially counteract ocean acidification associated with the current marked increase in atmospheric CO_2 , studies have reported that most of the additional C input to upstream rivers was either emitted back to the atmosphere as C dioxide ($\sim 0.4 \text{ Pg C y}^{-1}$) or sequestered in sediments ($\sim 0.5 \text{ Pg C y}^{-1}$)

along the continuum of freshwater bodies, estuaries, and coastal waters, leaving only a perturbation C input of $\sim 0.1 \text{ Pg C yr}^{-1}$ to the open ocean (Regnier et al. 2013).

Release of potential contaminants in surface waters as a result of accelerated weathering (Todd et al. 2012) and other climate-change related effects [e.g., the effect of warming temperatures on nitrate concentration of streams (Baron et al. 2009), and the hydrochemical effect of drought during hydrological episodes in streams (Laudon et al. 2004)], and the increase in surface water temperature [e.g., the increase in Columbia River water temperatures in response to climate change (Caldwell et al. 2013)] may significantly or even dramatically change elemental balances; affect microbially mediated reactions and processes occurring in rivers, lakes, and oceans; and/or affect aquatic life [e.g., may contribute to reduced fish survival and lower population productivity (Isaak, Wollrab, et al. 2012; Isaak, Muhlfield, et al. 2012; Zeigler et al. 2012).

Another recent study illustrated how changes in hydrologic regime may cause changes in biogeochemical processes that exacerbate the danger to aquatic ecosystems (Crouch et al. 2013). According to these authors, a major water quality concern in the Rocky Mountains is acid rock drainage, which causes acidic conditions and high metal concentrations in streams. They found the 30-year water quality record for the upper Snake River in Colorado to show that summer low-flow Zn concentrations have increased four- to six-fold concurrently with increases in mean annual and summer temperatures and a two- to three-week advancement in spring snowmelt. They also found that the main source of Zn and other metal loads to the upper Snake River is a tributary draining an alpine area rich in disseminated pyrite. The authors presented several potential explanations, all related to climate change, which might explain this phenomenon such as 1) decreasing pH in the tributary of interest resulting in mobilization of metals from the wetland and hyporheic zone; 2) the geochemistry of groundwater inflows to the wetland may be changing; and 3) wetland soils may be drying out with longer, warmer summers. Studies are needed to determine the magnitude and fate of various chemical elements released from weathering in different soils and under changing climate conditions.

Another extremely important topic is that climate change will affect groundwater resources and there is a need for quantitative predictions of climate-change effects on groundwater recharge, which may be valuable for effective management of future water resources (Crosbie et al. 2013). The study by Crosbie et al. (2013) reported that predicted changes in recharge between dry and wet future climate scenarios encompassed both an increase and decrease in recharge rates, with the magnitude of this range greater than 50% of the current recharge. Another study developed a new method for identifying triggers of hydrologic droughts by examining the association among various hydro-climatic variables and stream flows (Maity et al. 2013). These and other future studies are important for understanding how crucial water will be in agriculture and food production in a warming world. The impact of climate change on groundwater resources is an important topic that deserves full attention of the scientific community.

2.2.5 Coupled Cycles of C and Other Elements

The C cycle is coupled with the cycles of other elements that are commonly present in terrestrial systems, with Si being one of the elements. There are two important aspects of coupled Si-C cycling related to weathering of silicate minerals. The first aspect has to do with the fact that coupled Si-C cycles are driven by plant action and play a crucial role in the regulation of atmospheric CO_2 (Song et al. 2012). These authors claimed that the processes involved in the coupled cycles of these two elements included

plant-enhanced silicate weathering, phytolith formation and solubilization, secondary aluminosilicate accumulation, phytolith occlusion of C, and physico-chemical protection of OC in soils. They also claimed that there was increasing evidence of biological pumping of Si in terrestrial ecosystems, suggesting that complex feedback loops existed among the processes within the coupled Si-C cycles and offering promising new possibilities for enhancing atmospheric CO₂ sequestration. They concluded that organic mulching, rock powder amendment, cultivating Si-accumulating plants, and partial plant harvesting are potential measures that may allow for long-term manipulation and biogeochemical sequestration of atmospheric CO₂ in soil-plant systems (Song et al. 2012). Other studies emphasized the importance of Si-accumulating plants (e.g., grasses, sedges, palms; some temperate deciduous trees and conifers; and many tropical hardwoods), which deposited significant amounts of amorphous hydrated silica in their tissues as opal phytoliths (Street-Perrott and Barker 2008). This paper reviewed the biological role of Si in higher plants, the impact of vegetation on rates of chemical weathering, and the fluxes of Si through catchment ecosystems, lakes, and rivers. The authors stated that on geological time-scales, the global geochemical cycles of C and Si were coupled by the drawdown of atmospheric CO₂ through chemical weathering of Ca- and Mg-silicate minerals in continental rocks (Street-Perrott and Barker 2008), which is the second aspect of coupled Si-C cycling in soils [i.e., release of carbonate-forming cations such as Mg, Fe, and Ca and formation of carbonate minerals (see previous sections of this paper)].

2.3 Soil/Geo-engineering Techniques for C Sequestration

Over the last few years, a series of papers have been published about “enhanced weathering” (which is a term used to describe a soil/geo-engineering concept based on the process of soil-mineral weathering and carbonate precipitation) that is proposed to be used to reduce rising CO₂ levels by spreading fine-powdered olivine on farmland or forestland (Schuiling and Krijgsman 2006; Köhler, Hartmann and Wolf-Gladrow 2010; Köhler et al. 2011; Schuiling 2012; Schuiling et al. 2011; Olsson et al. 2012; Zevenhoven et al. 2011; King et al. 2010; Hartmann et al. 2013; ten Berge et al. 2012).

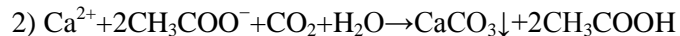
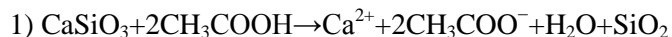
Enhanced weathering may sequester a significant amount of CO₂ in soils at relatively fast time-scales. Progress in this area of research has been encouraged by the slow deployment of large-scale underground storage of CO₂ and the fact that large amounts of suitable, relatively unstable, minerals and rocks are available worldwide (Zevenhoven, Fagerlund and Songok 2011). In addition, the method offers leakage-free CO₂ fixation that does not require post-storage monitoring (Zevenhoven, Fagerlund and Songok 2011). However, published studies on how efficiently this geo/soil-engineering approach would work in different soils and under different climate conditions are scarce.

Enhanced weathering, like natural weathering, involves the dissolution of Ca- and Mg-bearing silicate minerals and the subsequent release into the aqueous phase of Ca and Mg where they may react with dissolved CO₂ in the form of bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻) ions, to form carbonate minerals such as calcite (CaCO₃), magnesite (MgCO₃), and dolomite [CaMg(CO₃)₂] (Renforth 2012). Weathering and subsequent precipitation of Ca- and Mg-bearing carbonates are the main processes that contribute to CO₂ gas removal from the atmosphere (Schuiling and Krijgsman 2006). Artificially enhanced silicate weathering would not only operate against rising temperatures but would, indirectly, reduce ocean acidification, because it influences the global climate via the IC cycle (Köhler, Hartmann and Wolf-Gladrow 2010). These authors reported that the potential sequestration was up to 1 Pg C y⁻¹ if olivine would be distributed as fine powder in the humid tropic regions of the Amazon and Congo River

catchments, but they also emphasized that this causes pH values in the rivers to rise to 8.2, and the dissolution rate was limited by the saturation concentration of H_4SiO_4 . Other researchers claimed that the presence of a new Mg-silicate phase and the formation of secondary products at the olivine surface may limit the extent of olivine to carbonate conversion and understanding the relationship between the formation of carbonate and other phases is important for predicting the impact of possible passivating layers on the extent and rate of reaction (King, Plumper and Putnis 2010).

In another paper (Schuiling, Wilson and Power 2011), the authors disputed the conclusion by (Köhler, Hartmann and Wolf-Gladrow 2010) that the saturation of H_4SiO_4 would limit olivine dissolution. Schuiling et al. (2011) claimed that the H_4SiO_4 may be consumed abiotically [i.e., precipitation of opaline silica, quartz and/or formation of phyllosilicate clay minerals] and/or biotically [i.e., by vascular plants and diatoms in lakes and rivers] [(Schuiling, Wilson and Power 2011) and references therein]. Based on these arguments, Schuiling et al. 2011 claimed that the saturation concentration of H_4SiO_4 would be never reached during natural weathering of pulverized ultramafic rock. This is definitely an open discussion and further research efforts are needed. Additional information on the enhanced weathering geo-engineering approach can be found in other papers (Schuiling 2012; Schuiling and Krijgsman 2006; Renforth 2012; Hartmann et al. 2013; Moosdorf et al. 2014; Kojima et al. 1997; Lackner et al. 1995; Lackner et al. 1997; Power et al. 2013; Krevor and Lackner 2009; Ruiz-Agudo et al. 2013; Sissmann et al. 2014).

Another method to sequester atmospheric CO_2 via artificially accelerated weathering involves the following two steps (Kakizawa et al. 2001):



According to these authors, the first step was the extraction of Ca ions by acetic acid from Ca silicate (e.g., wollastonite). The second step was Ca carbonate precipitation promoted by the presence of CO_2 . Other recent studies have evaluated how alkaline silicate mineral-based CO_2 sequestration can be achieved using environmental biotechnological processes that involve an acid-producing reaction to enhance silicate dissolution and a subsequent alkalinity-producing step to precipitate carbonates (Salek et al. 2013).

In concluding this discussion about enhanced weathering of silicate minerals as a method for sequestering atmospheric CO_2 concentration, one should emphasize that many issues related to weathering rates in different soils and conditions and impacts to soils and water resources are not fully understood, and further investigation in this area is required to reduce the many uncertainties associated with this method.

3.0 Climate-Change Induced SOM Transformation and Mineralization

3.1 SOM in Soils

The organic matter content of soils is one of the most important soil properties that define soil fertility and, to a large extent, control the chemical and biological behavior of the soil system. For this reason, different aspects of SOM formation, transformation, mineralization, and interaction with soil minerals or other organic molecules have attracted the attention of many soil scientists over the last decades. However, although this is a relatively well explored area of research, SOM studies at the molecular, nano, and micron scales have intensified especially in recent years because of technological advances and the relevance to climate change, which is expected to affect in unprecedented ways the life on earth.

Organic C incorporated into SOM may play a major role in controlling soil behavior as a sink or source for atmospheric CO₂ (Ghee et al. 2013), thus contributing significantly to the global C cycle. Because of predicted climate change and the need for a more unified approach to mitigate greenhouse gas emissions, the soil's ability to sequester and/or release C into atmosphere, and thus to act as a C sink or source for atmospheric CO₂, has received growing attention (Solomon et al. 2012). For example, enhanced soil respiration in response to global warming may substantially increase atmospheric CO₂ concentrations above the anthropogenic contribution, depending on the mechanisms underlying the temperature sensitivity of soil respiration (Tucker et al. 2013). The uncertainty associated with how projected climate change will affect global C cycling could have a large impact on predictions of soil C stocks (Haddix et al. 2011) and the long-term changes in soil OC storage (Conant et al. 2011).

A new set of scientific questions have surfaced recently about the soil sink/source behavior and the effects of climate-change variables on the positive or negative CO₂ gas fluxes between terrestrial systems and atmosphere, and other important soil processes and reactions. In addition, climate-change variables may induce significant or even dramatic shifts in SOM budgets and distribution among different pools, with short- and long-term effects that are currently unknown. To address these and other related questions and uncertainties, an increasing number of scientists from different disciplines and communities are using state-of-the-art microscopic and spectroscopic techniques (Remusat et al. 2012; Kleber et al. 2011; Vogel et al. 2014; Kaiser and Guggenberger 2007; Solomon et al. 2012; Kinyangi et al. 2006; Solomon et al. 2007; Lehmann et al. 2008; Erhagen et al. 2013) with the objective of improving our understanding of different aspects of SOM transformations and interactions within soil matrices. To address emerging issues in these research areas, scientists also are using a variety of research instruments that would allow interrogations of soils and SOM under transient dynamic conditions [e.g., dynamic transmission electron microscopy (DTEM) used in studies conducted at the Environmental Molecular Science Laboratory in Richland, Washington); instruments that can probe SOM heterogeneities at incredibly small spatial resolutions (Milne et al. 2011; Lehmann et al. 2008) and extremely fast temporal scales (involving DTEM); and sophisticated geostatistical models such as those used to study spatial distribution of soil organic carbon (SOC) at large scales (Martin et al. 2014), or other models such as the Dual Arrhenius and Michaelis-Menten kinetics models (Davidson et al. 2012; Paterson and Sim 2013).

This section is not intended to be a comprehensive review, but instead presents a focused effort on a variety of recent developments and an attempt to uncover emerging and/or unresolved research gaps on the effects of climate-change variables on SOM budgets and pools, protection, mineralization, and

temperature sensitivity. The reader is referred to a number of recent review papers for an in-depth coverage and discussion on 1) the evolution of concepts of the chemical and physical nature of SOM and arguments that have led to increased skepticism about the humification concept and usefulness of operationally defined “humic substances” (Kleber and Johnson 2010); 2) the amount of C stored in soils globally, the potential for C sequestration in soil, and successful methods and models used to determine and estimate C pools and fluxes (Stockmann et al. 2013); 3) SOM characterization, isolation and fractionation, pools, and formation of recalcitrant components of SOM (Maia et al. 2013); 4) earth science models that should simulate microbial physiology to more accurately project climate-change feedbacks (Wieder et al. 2013); 5) methods used to characterize SOM structure, source, and degradation that have enabled precise observations of SOM and associated ecological shifts (Simpson and Simpson 2012); 6) some important and challenging aspects of soil extracellular enzyme research (Burns et al. 2013); 7) SOC sequestration under different tillage systems in China (Zhang et al. 2014); 8) the pool of thaw-vulnerable OC of the permafrost based on field data and extrapolation using geospatial data (Strauss et al. 2013); and 9) impact of permafrost thaw on OM chemistry which could intensify the predicted climate feedbacks of increasing temperatures, permafrost C mobilization, and hydrologic changes (Hodgkins et al. 2014).

3.1.1 SOM Budget and Pools

Globally, a significant C amount is stored in the world’s soils, including peatlands, wetlands, and permafrost (Davidson and Janssens 2006; von Lutzow and Kogel-Knabner 2009; van Groenigen et al. 2014). On a global scale, soils contain approximately 2344 Pg C in the top 3 m of soil, with about 1502 Pg in the first meter, and 491 and 351 Pg C for the second and third meters, respectively (Jobbagy and Jackson 2000). In addition, SOM contains more than three times as much C as either the contemporary atmosphere or terrestrial vegetation (Schmidt et al. 2011; Erhagen et al. 2013); therefore, even small changes to its inventory may have major implications for atmospheric CO₂ concentrations (Erhagen et al. 2013; Stockmann et al. 2013; van Groenigen et al. 2014). Clearly, soils may play a key role in modulating climate change (van Groenigen et al. 2014). For this reason, our ability to predict and ameliorate the consequences of global warming depends in part on a better understanding of the distributions and controls over SOM (Jobbagy and Jackson 2000).

The SOM originates from different sources such as residues from plant, microbes, or other living organism in soils and, chemically, is a complex mixture of many organic compounds. Even when it originates from the same source, the chemical composition of the SOM is remarkably diverse. For example, plant residues often are complex mixtures of mainly polysaccharides [i.e., starch, cellulose, hemicellulose and pectin (50–60%); lignin (15–20%), polyphenols (e.g., tannins), chlorophyll, cutin and suberin, lipids and waxes (10–20%)] (von Lutzow et al. 2006). These organic compounds may have different fates and follow different transformation pathways, further contributing to SOM chemical composition diversity. A critical examination of published data obtained from many molecular-scale studies revealed that humic substances are diverse with components spatially segregated at the nanometer scale (Sutton and Sposito 2005). Other studies have found that humic substances, which represent the largest pool of recalcitrant SOM in the terrestrial environment, are a very complex mixture of microbial and plant biopolymers and their degradation products that do not represent a distinct chemical category (Kelleher and Simpson 2006). This is the main reason why SOM pools are difficult to define based on the chemistry and/or molecular identity of the organic compounds that are present in these pools.

Nevertheless, for modeling and investigative purposes, SOM pools are operationally defined as 1) a labile pool (short residence time) and 2) a recalcitrant (refractory) pool (long residence time), which includes humin, and fulvic and humic acids. Based on the stabilization and protection mechanisms, SOM pools are defined as 1) unprotected; 2) physically protected from decomposition via micro-aggregation; 3) stabilized via intimate association with soil fine fractions (silt and clay); and 4) biochemically stabilized through the formation of recalcitrant SOM compounds; each of these pools behaves differently in terms of extent and rate of decomposition (Six et al. 2002), but their individual and combined contributions to the CO₂ gas flux coming out of soils, remains unclear.

As the largest pool of terrestrial OC, soils interact strongly with atmospheric composition, climate, and land cover changes (Jobbagy and Jackson 2000). If C stored belowground is transferred to the atmosphere by a warming-induced acceleration of its decomposition, a positive feedback to climate change would occur (Davidson and Janssens 2006). Conversely, if increases of plant-derived C inputs to soils exceed increases in decomposition, the feedback to climate change would be negative (Davidson and Janssens 2006). The fluxes of SOC vary in response to a host of potential environmental and anthropogenic driving factors and important questions have been raised, such as (Stockmann et al. 2013):

- What is the average net change in SOC due to environmental conditions or management practices?
- How can SOC sequestration be enhanced to achieve atmospheric CO₂ mitigation?
- Will this secure soil quality and preserve soil resources so that they will provide sufficient food and fiber to a growing world population?

The first and the second questions were addressed in a study conducted at Rothamsted (United Kingdom) (Fornara et al. 2011). In that study, the researchers investigated the combined effect of liming on microbial respiration and net OC accumulation using experimental data spanning 129 years. They found that liming contributes to higher rates of respiration from soil (thereby potentially reducing soils ability to act as a CO₂ sink; however, it stimulated biological activity that, despite increasing soil respiration rates, led to plant C inputs being processed and incorporated into resistant soil organo-mineral pools, shielding SOM from weathering. The net OC sequestration reported in this study, measured in the 0–23 cm soil layer at different time intervals since 1876, was 2–20 times greater in limed than in unlimed soils). The authors concluded by stating that the greater OC sequestration in limed soils strongly reduced the global warming potential of long-term liming to permanent grassland suggesting the net contribution of agricultural liming to global warming could be lower than previously estimated (Fornara et al. 2011). Their study demonstrated that the common agricultural practice of applying lime might be an effective mitigation strategy especially because it can be associated with a reduced use of nitrogen (N) fertilizers, which are a key cause of increased greenhouse gas emissions from agro-ecosystems (Fornara et al. 2011). This example clearly illustrates that changes in soil inorganic chemistry may have significant impacts on OC storage and its distribution or redistribution within pools in which it has become less bioavailable.

A few studies have addressed issues related to the SOM budget under climate-change conditions (i.e., atmospheric CO₂ enrichment, intensive precipitation or prolonged drought, higher temperatures and heat waves) and different soil management approaches. One study was conducted with soils from the U.S. Great Plains, which contained enormous stocks of SOC and soil organic nitrogen (SON) that would be vulnerable to predicted climate and land use changes (Follett et al. 2012). The authors found that soil C and N stocks under different land uses were equally vulnerable to increased temperature and decreasing water availability. They reported that an increase in mean annual temperature of 1°C (1.8°F) could cause

a loss of 486 Tg SOC and a loss of 180 kg SON ha⁻¹ from the top 10 cm of soil over 30 years. They concluded that combined increased temperature and conversion from the conservation program to cropland could decrease the existing SOC pool sink, but improved soil management and increased water availability may help offset these losses in the U.S. Great Plains (Follett et al. 2012). Most C stocks in soils are comprised of SOM with turnover times of decades to centuries, and understanding the response of these C pools to climate change is essential for predicting longer-term changes in soil C storage (Conant et al. 2011). However, additional and much broader efforts are required to fully address the question posed above.

The SOM turnover times may be accelerated because of increasing CO₂ concentration in the atmosphere as it was demonstrated in a study that investigated the effect of rising atmospheric CO₂ on combined responses of stimulated plant growth (which result in soil C addition) and microbial decomposition (which result in soil C removal) (van Groenigen et al. 2014). The results showed that atmospheric CO₂ enrichment stimulates both the input of C in soil (+19.8%) and the turnover of C in soil (+16.5%) (van Groenigen et al. 2014). They also reported that the increase in soil C turnover with rising CO₂ led to lower equilibrium soil C stocks than expected from the increase in soil C input alone, indicating that the net outcome of these combined effects was negative and results in a general mechanism that limits C accumulation in soil (van Groenigen et al. 2014). This pioneering study should be followed by many more so other important aspects of soil and ecosystem response to climate change will be elucidated.

3.1.2 SOM Saturation Limit

One important concept related to the soil C budget concerns soil finite capacity or soil OC saturation limit and SOM dynamics within the framework initially described by Six et al. (Six et al. 2002) and explored further in other studies (Stewart et al. 2007; Stewart, Plante, et al. 2008; Stewart, Paustian, et al. 2008; Qin et al. 2013; Feng et al. 2014). Soil OC saturation behavior predicts that soil OC storage efficiency observed under field conditions decreases as the soil approaches OC saturation (Six et al. 2002). These authors suggested that physicochemical characteristics inherent to soils usually define the maximum protective capacity for SOM, and limit increases in SOM (i.e., C sequestration) with increased organic residue inputs (Six et al. 2002). Other authors have noticed that current estimates of soil OC storage potential are based on models or factors that assume linearity between OC input levels and OC stocks at steady-state, implying that SOC stocks could increase without limit as C inputs increase (Stewart et al. 2007). In their long-term field experiments, these authors found that some soils showed little or no increase in steady-state SOC stock with increasing C inputs, suggesting saturation. In this and other studies, the authors concluded that the saturation of soil OC did occur, and therefore, the greatest efficiency in soil C sequestration will be in soils further from OC saturation (Stewart et al. 2007), or in soils with low OC contents and in degraded lands (Stewart, Paustian, et al. 2008).

In another study (Stewart, Plante, et al. 2008), four different soil OC pools [e.g., unprotected (free particulate organic matter); physically protected (microaggregate-associated C); chemically protected (silt- and clay-associated C), and biochemically protected (non-hydrolyzable C)] were considered. These authors assessed two contrasting models of SOC accumulation, one with no saturation limit (i.e., linear first-order model) and one with an explicit soil OC saturation limit (i.e., C saturation model). They found that the two sites with the greatest SOC range showed OC saturation behavior in the chemically,

biochemically, and some mineral-associated pools of the physically protected pool. Importantly, the unprotected pool and the aggregate-protected showed linear, non-saturating behavior.

Evidence of C saturation of chemically and biochemically protected SOC pools was observed at sites far from their theoretical OC saturation level, while saturation of aggregate-protected pools occurred in soils closer to their OC saturation level (Stewart, Plante, et al. 2008). In a more recent study, data from worldwide, long-term agricultural experiments were used to develop two statistical models to determine the saturated SOC level in upland and paddy agro-ecosystems (Qin, Huang and Zhuang 2013). These authors found that Chinese croplands had relatively low SOC contents in comparison to the global average and great potential for C sequestration under improved agricultural management strategies; the time required to reach SOC saturation in Chinese cropland was highly dependent on the management practices applied (Qin, Huang and Zhuang 2013).

Based on the assumption that soil OC saturation behavior predicts that soil OC storage efficiency observed under field conditions decreases as a soil approaches C saturation, other researchers have hypothesized that this may be due to a decline in SOM stability as the result of changes in the type, strength, or turnover time of organo-mineral interactions with increasing organic C input (Feng et al. 2014). However, results from a series of batch sorption experiments did not support the hypothesis that SOM stability decreases with increasing C loading.

The concept of C saturation is called into question in a recent study by Vogel et al. (Vogel et al. 2014). The results from this study provided evidence that only a limited proportion of the clay-sized surfaces contributed to OM sequestration, providing a different view of C sequestration in soils and the widely used C saturation estimates (Vogel et al. 2014).

3.1.3 SOM Accumulation in Subsoil

Conceptual models developed based on results collected from many studies conducted with soils from different regions consider that the stability of SOM depends, among other factors, on location within the soil profile. Studies have confirmed that the subsoil OC pool is significant. The percentage of SOC in the top 20 cm (relative to the first meter) averaged 33%, 42%, and 50% for shrublands, grasslands, and forests, respectively (Jobbagy and Jackson 2000). In shrublands, the amount of SOC in the second and third meters was 77% of the amount found in the first meter; in forests and grasslands, the totals were 56% and 43%, respectively (Jobbagy and Jackson 2000). These results clearly demonstrate the tendency of the SOC to accumulate (i.e., stabilize) in the subsoil.

Results from other studies have shown that the relevance of spatial inaccessibility and organo-mineral interactions for SOM stabilization increased especially in subsoil (von Lutzow et al. 2006). However, the reasons for enhanced OC stabilization in subsoil horizons are currently poorly understood (Chabbi et al. 2009), and whether the stabilization mechanisms are different in subsoil than topsoil remains unresolved. Some other important scientific issues related to SOM accumulation in subsurface, C cycling and climate change are identified and discussed below:

1. *How is SOM transported from topsoil to subsoil?* Ideas on how SOM is transported from topsoil to subsoil, in addition to the most common mode of transportation (i.e., DOM moving down the soil profile with advective flow), were presented in a few recent studies. For example, one study found that long-term C storage in short-range ordered minerals occurred via chemical retention with

dissolved aromatic acids derived from plant litter, which were carried along preferential flow-paths to deeper B horizons (Kramer et al. 2012). Another study, conducted with basaltic soils from Hawaii exposed to high rainfall and anoxic conditions that facilitated Fe(III) (oxyhydr)oxide reductive dissolution (i.e., climate-controlled redox dynamic condition), showed that colloidal dispersion during Fe-reducing conditions mobilized high concentrations of C from the pool of C strongly associated with the Fe(III) phases, which may then migrate to deep mineral horizons (Buettner et al. 2014).

2. *How can SOM spatial heterogeneity and the effects of hydrology be characterized and represented in models and how would this vary as a function of the scale of the models?* The effect of hydrology and heterogeneous distribution on SOM preservation in subsoil was investigated in a paper by Chabbi et al., 2009. In the subsoil of three agricultural lands, compartments of visually identifiable zones in the form of tongues (with modern age SOM) and the adjacent soil matrix (with several thousand-year-old SOM) were present in deep soil horizons (60-140 cm depth) (Chabbi, Kogel-Knabner and Rumpel 2009). The results indicated that tongues had two times higher C content and were depleted in N with regards to the adjacent soil matrix. Twenty percent more hydrofluoric-acid soluble C was in the soil matrix compared to tongues. The authors of this study suggested that, in tongues, fresh C input by preferential flow and/or roots led to higher SOM turnover compared to the soil matrix. The effect of hydrology and heterogeneous distribution of stabilized SOM within the subsoil matrix must be taken into account when studying C sequestration in deep soil horizons (Chabbi, Kogel-Knabner and Rumpel 2009).
3. *What is the SOM stabilization mechanism in subsurface?* Studies about SOM stabilization mechanisms have shown that OC stability in deep soil layers depends on the supply of fresh plant-derived C to the subsoil, which stimulated the microbial mineralization of 2567 ± 226 -year-old C (Fontaine et al. 2007). These results supported the idea that, in the absence of fresh OC (an essential source of energy for soil microbes), the stability of OC in deep soil layers was maintained (Fontaine et al. 2007). Other studies have also shown that SOM mineralization in many soils generally increased after addition of carbohydrates, amino acids, or simple organic acids, thus indicating that stability may be caused by substrate limitations (Marschner et al. 2008). Under climate-change conditions, a lack of supply of fresh OC may prevent the decomposition of the SOM in deep soil layers in response to temperature changes. On the other hand, intensive rainfall and soil management practices, such as changes in land use and application of different agricultural practices that increase the distribution of fresh C along the soil profile, may stimulate the loss of ancient buried C (Fontaine et al. 2007).
4. *What is the role of subsurface naturally reduced zones (NRZ) or other organic-rich systems on C and elemental cycling?* NRZs represent a SOM pool common in many environments. Subsurface NRZs are characterized by transient anaerobic and aerobic conditions and are places where the biogeochemical cycles of C and other elements (such as Fe) or contaminants (such as U) are strongly interlinked and overlap in remarkable and rather complex ways (Qafoku et al. 2009; Campbell et al. 2012; Qafoku et al. 2014). There are examples in the literature showing how cycling of other elements affect the C cycle other organic-rich systems (e.g., humid tropical forests), similar to NRZs. A recent study found that microbial Fe reduction generated reduced Fe^{2+} under anaerobic conditions, which oxidized to Fe^{3+} under subsequent aerobic conditions (Hall and Silver 2013). These authors demonstrated that Fe^{2+} oxidation stimulated SOM decomposition via two mechanisms: 1) OM oxidation [via generation of reactive O_2 species during Fe^{2+} oxidation] and 2) increased DOC availability [via proton generation during Fe^{2+} oxidation] (Hall and Silver 2013). This study concluded that Fe oxidation coupled to SOM decomposition contributed to rapid rates of C cycling

across humid tropical forests in spite of periodic O₂ limitation, and may help explain the rapid turnover of complex C molecules in these soils (Hall and Silver 2013). Coupling of C and Fe cycles also is common in marine sediments as well, where the associations between OC and Fe formed primarily through co-precipitation and/or direct chelation promote the preservation of OC in sediments of various mineralogy from a wide range of depositional marine environments (Lalonde et al. 2012).

5. *What is the sensitivity of subsoil SOM to global change drivers?* The sensitivity of SOC at different soil depths to global change drivers is another topic receiving increasing attention because of its importance in the global C cycle and its potential feedback to climate change (Albaladejo et al. 2013). According to these authors, the relative importance of climatic factors decreased with increasing depth, and soil texture became more important in controlling SOC in all land uses (Albaladejo et al. 2013). Because of climate change, impacts will be much greater in surface SOC, so the strategies for C sequestration should be focused on subsoil sequestration, which was hindered in forestland due to bedrock limitations to soil depth. In these conditions, sequestration in cropland through appropriate management practices was recommended (Albaladejo et al. 2013). A better knowledge of the vertical distribution of SOC and its controlling factors will help scientists predict the consequences of global change (Albaladejo et al. 2013).

Other factors that may control SOM distribution with depth and its preservation are vegetation, soil types, parent material, and land use (Schrumpf et al. 2013); no-tillage management as a practice capable of offsetting greenhouse gas emissions and its ability to sequester C in soils combined with improved N management techniques (Six et al. 2004); and changes in tropical land use and cultivation to control SOM status in subsoil because cultivation modifies the distribution of the more labile fractions of the SOM (Guimaraes et al. 2013).

3.2 SOM Protection Mechanisms

Mechanisms and pathways of SOM stabilization have received increasing attention recently because of their relevance in the global C cycle and global warming. The following discussion will be focused on these and other stabilization mechanisms, and a variety of scientific issues related to SOM stabilization and mineralization in soils under conditions imposed by the climate change.

Numerous attempts have been made to understand SOM protection mechanisms that operate in different soils and under different conditions (Six et al. 2002; von Lutzow et al. 2006; Schrumpf et al. 2013). The predominant SOM protection mechanisms in temperate soils, discussed in a comprehensive publications by von Lutzow et al. (von Lutzow et al. 2006) are:

1. selective preservation due to structural composition including plant litter, rhizodeposits, microbial products, humic polymers, and charred OM;
2. spatial inaccessibility of SOM against decomposer organisms due to occlusion, intercalation, hydrophobicity and encapsulation; and
3. stabilization by interaction with mineral surfaces (Fe, Al, Mn oxides, and phyllosilicates) and metal ions (von Lutzow et al. 2006). The protection mechanisms may also operate simultaneously at different stages of SOM decomposition (von Lutzow et al. 2006), and may be a function of site-

specific, spatial- and time-dependent dynamic conditions that often are combined with complex scale-dependent effects.

3.2.1 Selective Preservation

When it comes to the stabilization mechanisms of SOM as a complex mixture of identifiable biopolymers (Kelleher and Simpson 2006) rather than a chemically complex material (such as humic and/or fulvic acids), one of the predominant arguments for many years has been about the resistance of SOM to mineralization, and whether this apparently inherent chemical or biochemical property makes some SOC's more resistant than others so that they are selectively preserved. The paradigm of what is called “intrinsic recalcitrance” is therefore based on the idea that some naturally occurring organic molecules in soils can resist decomposition because of thermodynamic stability and/or their unique and resistant molecular structure.

Traditionally, the selective preservation of certain recalcitrant organic compounds and the formation of recalcitrant humic substances have been regarded as an important mechanism for SOM stabilization (Marschner et al. 2008). Solid-state ^{13}C nuclear magnetic resonance studies suggested that the most persistent mineral-bound C was composed of partially oxidized aromatic compounds with strong chemical resemblance to DOM derived from plant litter (Kramer et al. 2012). In addition, soil C turnover models generally divided SOM into pools with varying intrinsic decomposition rates based on the assumption that the chemical structure had primary control over decomposition (Kleber et al. 2011). One should emphasize, however, that determining recalcitrance through experiments is difficult because the persistence of certain SOM pools or specific compounds also may be the result of other stabilization mechanisms, such as physical protection or chemical interactions with mineral surfaces (Marschner et al. 2008).

Some authors have recently disputed the view that SOM stabilization is dominated by the selective preservation of recalcitrant organic components that accumulate in proportion to their chemical properties (von Lutzow et al. 2006). In contrast, they have shown that the soil biotic community is able to disintegrate any organic compound, making the molecular recalcitrance of SOM relative rather than absolute (von Lutzow et al. 2006). In a recent paper by Kleber (Kleber 2010), the author argued that “... recalcitrance is an indeterminate abstraction whose semantic vagueness encumbers research on terrestrial C cycling.” The author proposed a different view to the perceived “inherent resistance” to decomposition not as a material property, but as a logistical problem constrained by 1) microbial ecology, 2) enzyme kinetics, 3) environmental drivers, and 4) matrix protection (Kleber 2010). A consequence of this view would be that the frequently observed temperature sensitivity of SOM decomposition will result from factors other than intrinsic molecular recalcitrance (Kleber 2010; Kleber and Johnson 2010).

In a follow-up study, near edge X-ray absorption fine structure (NEXAFS) spectroscopy was used in combination with differential scanning calorimetry (DSC) and alkaline cupric oxide (CuO) oxidation to test the hypothesis whether the chemical structure has primary control over decomposition (Kleber et al. 2011). This study found that the SOM of an Inceptisol, with a ^{14}C age of 680 years, had the largest proportion of easily metabolizable organic molecules with low thermodynamic stability, whereas the SOM of the much younger Oxisol (107 years) had the highest proportion of supposedly stable organic structures considered more difficult to metabolize. The authors suggested that soil C models would

benefit from viewing turnover rate as co-determined by the interaction between substrates, microbial actors, and abiotic driving variables.

3.2.2 Spatial Inaccessibility

The second SOM protection mechanism has to do with the fact that the SOM can be spatially inaccessible and, as a result, unavailable to decomposer organisms due to occlusion, intercalation, hydrophobicity, and encapsulation (von Lutzow et al. 2006).

Occluded SOM is spatially protected due to reduced access for microorganisms and enzymes, reduced diffusion of enzymes within the intra-aggregate space, and reduced diffusion of O₂ responsible for the aerobic decomposition of the SOM (von Lutzow et al. 2006). The inter- and intra-aggregate pore-size distribution and SOM occurrence location (either close to the entry of the pores or deep in the remote sites) within aggregates plays an important role in the physical protection of the SOM. However, the size of the pores seems to play an important protective role because the formation of multiple complex bonds per molecule is possible and favored in small pores (Kaiser and Guggenberger 2007). A study conducted with microporous goethite demonstrated that the SOM tightly bound via multiple complex bonds, most likely at the entry of small pores, were resistant to desorption and attack of chemical reagents and probably enzymes (Kaiser and Guggenberger 2007). Another study demonstrated the role of spatial connectivity and pore-size distribution within the intra-aggregate space in affecting the ability of macro-aggregates to physically protect C (Ananyeva et al. 2013). **Intercalation** has to do with SOM sorption into interlayer space of expandable phyllosilicates, a protection mechanism that is operational especially in acidic soils (von Lutzow et al. 2006). However, Eusterhues et al. (2003) found no evidence of intercalated SOM into interlayer spaces of phyllosilicates in two German acid forest soils. Currently, a method has yet to be developed to probe the interlayer space of expandable phyllosilicates for intercalated SOM (Leifeld and Kögel-Knabner 2001). **Hydrophobicity** is another important factor to be considered as one of the SOM protection mechanisms because it may result in decreasing SOM decomposition rates and enhanced aggregate stability [(von Lutzow et al. 2006) and references therein]. Finally, another SOM protection mechanism is the one that involves labile organic matter **encapsulated** inside recalcitrant compounds although evidence of the occurrence of encapsulation is limited [(von Lutzow et al. 2006) and references therein]. It is challenging, however, to prove that this mechanism occurs in soils and advanced research techniques definitely need to be employed for these studies.

3.2.3 Interaction with Minerals

A third protection mechanism is that of SOM stabilization via interactions with mineral surfaces (such as Fe, Al, Mn oxides, and phyllosilicates) and metal ions (von Lutzow et al. 2006). Adsorption of SOM to fine soil particles, most frequently clay-sized particles [or even terrestrial nano-particles (Qafoku 2010)], is a well-known phenomenon occurring commonly in soils. The organo-mineral assemblages are even considered as a separate pool in mineral horizons of forest soils (Gruneberg et al. 2013). In some instances, the SOM consists of a heterogeneous mixture of compounds that display a range of amphiphilic or surfactant-like properties, and are capable of self-organization in aqueous solution (Kleber et al. 2007); however, the adsorption properties of these organic mixtures to soil minerals have not been well studied.

The fundamental aspects of SOM sorption to soil minerals, stabilization, and preservation are demonstrated by a substantial decrease in biological degradability after SOM is sorbed to mineral surfaces

(Kaiser and Guggenberger 2000; Zech et al. 1997; Kaiser and Guggenberger 2003; Kaiser et al. 2007; Lopez-Sangil and Rovira 2013). Strong correlations between Fe oxides and SOMs have implied the importance of the former in stabilizing the latter (Wagai and Mayer 2007). Other studies have investigated SOM sorption to soil minerals such as Al and Fe oxyhydroxides (Kaiser and Guggenberger 2000); amorphous Al(OH)₃; gibbsite, ferrihydrite, goethite, hematite, and phyllosilicates (kaolinite, illite) (Kaiser and Guggenberger 2003); and ferrihydrite and goethite (Kaiser, Mikutta and Guggenberger 2007). Studies have also looked at binding of lignin from three litters (blue oak, foothill pine, and annual grasses) to five minerals (ferrihydrite, goethite, kaolinite, illite, montmorillonite) (Hernes et al. 2013); and protein, lipid, carbohydrate, oxidized lignin, and carboxyl/carbonyl content interaction with short-range order minerals in soils from Hawaii (Kramer et al. 2012). Finally, studies on fractionation procedures capable of assessing the strength through which mineral-associated SOM is stabilized (Lopez-Sangil and Rovira 2013) may be useful in elucidating SOM interactions and affinity for different minerals in soils.

Because the SOM content in soils is usually positively related to the reactive surface area (Kaiser and Guggenberger 2003), quite often the soil clay content or reactive surface area has been used to estimate the SOM sequestration potential of soils (Vogel et al. 2014). However, only a relatively small portion (i.e., less than 19%) of the clay-sized surfaces of the topsoil binds SOM (Vogel et al. 2014). This study also showed that the new SOM added into the system was preferentially attached to already present organo-mineral clusters with rough surfaces (Vogel et al. 2014) and did not bind to other, apparently available mineral surfaces, indicating that surface properties were more important than the reactive surface area or soil texture, a concept that also was discussed in earlier studies (Kaiser and Guggenberger 2000; Plante et al. 2006).

The increase in SOM stability after interacting with soil minerals was shown in a series of incubation experiments conducted with SOMs of different origins sorbed to a subsoil material (Kalbitz et al. 2005). They found that the fraction of sorbed OC mineralized was much less than the fraction of the same identity in solution (in the absence of solids). They also estimated that the mean residence time of the most stable SOM was increased from 28 years in solution to 91 years after sorption. Different hypotheses have been tested in recent studies with the ultimate goal to determine the mechanistic aspects of SOM protection via interactions with soil minerals. The three-way correlation among SOM concentrations, specific surface areas, and small mesopores observed for many soils and sediments led researchers to develop the hypothesis that enclosure within the relatively small pores might explain the apparent protection of SOM by minerals (Mayer et al. 2004). They tested this hypothesis by examining whether the bulk of SOM resides within small mesopores. They found that, although smaller mesopores have sufficient volumes to contain significant fractions of the total OM, only small fractions of OM reside in them. They also found that OM was preferentially associated with aluminous clay particle edges rather than the largely siliceous clay faces that contribute most surface area and form pore walls. They concluded that, while simple enclosure within smaller mesopores cannot explain protection, network effects working at larger size scales may account for exclusion of digestive agents, resulting in OM protection (Mayer et al. 2004).

In another study (Wagai and Mayer 2007), the authors tested the hypothesis that sorption was important in the stabilization of SOMs by reductively dissolving Fe oxides in a wide variety of soils and measuring OC that was subsequently released. They found that the resultant pool, reductively soluble OC, made up a minor amount of total soil OC in all but one of these soils, indicating that simple sorption reactions do not stabilize the bulk of soil OC in most mineral soils and that SOM stabilization may occur via other mechanisms, such as organo-Fe oxide precipitates (see below) or ternary associations among Fe

oxides, the SOM, and other minerals. However, the scientific question regarding why and how OM matter is protected from decomposition when it is associated with minerals in soils still has not been answered.

Sorptive stabilization as a function of SOM chemical composition is another important topic. The extent of sorption of recalcitrant compounds was much larger than sorption of labile compounds (Kalbitz et al. 2005). These authors claimed that stabilization of OM by sorption depended on the intrinsic stability of organic compounds sorbed and that the main stabilization processes were selective sorption of intrinsically stable compounds and strong chemical bonds to the mineral soil and/or a physical inaccessibility of OM to microorganisms (Kalbitz et al. 2005). Other researchers claimed that because sorption of the more labile polysaccharide-derived DOM on mineral surfaces is weaker, adsorptive and desorptive processes strongly favored the accumulation of the more recalcitrant lignin-derived SOM in soils (Kaiser and Guggenberger 2000). Additional research is definitely needed to address the issue of increases in stability due to sorption and to show abiotic control on the mineralization rate of the sorbed SOM.

Types of binding mechanisms of SOM with minerals are another important issue that deserves more attention. Sorption of DOM derived from the oxidative decomposition of lignocellulose to Al and Fe oxyhydroxides involves strong complexation bonding between surface metals and acidic organic ligands, particularly with those associated with aromatic structures (Kaiser and Guggenberger 2000). Once DOM is sorbed on mineral surfaces, the desorption of a large part of sorbed DOM is almost fully irreversible under conditions similar to those of adsorption, but it also depends on the surface properties of the sorbate (Kaiser and Guggenberger 2000). A spectroscopic study showed that there is an enormous complexity of the OC functionalities and various inorganic components in the organo-mineral assemblages and interfaces, and it is likely that no single binding mechanism could be accountable for the organic C stored at the micron scale (Solomon et al. 2012). The researchers in this study suggested that the apparent C sequestration at this scale was due to both the cumulative result of physical protection and heterogeneous binding mechanisms (i.e., ion exchange, hydrogen bonding, and hydrophobic bonding) on silicate clay organic complexes and adsorption on external and internal surfaces of clay minerals. Another study reported that sorbed SOM may undergo changes in configuration or may migrate into intra-particle spaces with time after sorption (Kaiser, Mikutta and Guggenberger 2007). These researchers investigated the effects of the residence time of SOM sorbed onto ferrihydrite and goethite and found that with increasing residence time, SOM sorbed to porous minerals becomes decreasingly desorbable because of formation of additional chemical bonds to the surface. Additional studies are needed to investigate different SOM binding mechanisms to minerals and the effects of climate-change variables on these mechanisms.

The soil mineral-sorbed OM interface is very important in terms of understanding SOM stability in natural heterogeneous systems. This interface has been conceptualized as a discrete zonal sequence (Kleber, Sollins and Sutton 2007). In the first contact zone, either stable inner-sphere complexes are formed as a result of ligand exchange between organic functional groups and mineral surface hydroxyls, or proteinaceous materials unfold upon adsorption increasing adhesive strength by adding hydrophobic interactions to electrostatic binding. The second zone is formed when exposed hydrophobic portions of amphiphilic molecules of the first contact zone are shielded from the polar aqueous phase through association with hydrophobic moieties of other amphiphilic molecules. The components of the second zone may exchange more easily with the surrounding soil solution than those in the contact zone, but are still retained with considerable force. The third zone, or kinetic zone, contains organic molecules forming an outer region that is loosely retained by cation bridging, hydrogen bonding, and other interactions. The authors of this model (Kleber, Sollins and Sutton 2007) claimed that the zonal concept of organo-mineral

interactions offered a new basis for understanding and predicting the retention of organic compounds, including contaminants, in soils and sediments. While the zonal concept is extremely useful (apparently, it is the only model that provides a clear picture of the solid surface-solution interface during OM adsorption), additional experimental confirmation of this model is needed. In addition, the implications of this model for stability of SOM during climate change, especially the impact of higher heat levels on the binding processes in the different zones, are not well understood.

Spectroscopic investigations of the SOM spatial heterogeneity at the molecular scale and the nano-scale demonstrate the existence of highly variable, spatially distinct, micro- and nano-C repository zones, where OC is sequestered in agglomerated organo-mineral assemblages (Lehmann et al. 2008; Solomon et al. 2012). These submicron-C repositories have considerably different compositions, indicating a high degree of spatial heterogeneity at the micrometer scale (Solomon et al. 2012).

The spectroscopic investigations also showed that the interfacial chemistry of the organo-mineral assemblages was extremely complex, ranging from Ca, Fe, and Al ions; Fe and Al oxides; hydroxides and oxyhydroxides; to phyllosilicates, which could provide a variety of polyvalent cations, hydroxyl surface functional groups, and edge sites that can bind organic compounds (Solomon et al. 2012). Given the complex nature of the interface between the mineral surface adsorbed SOM, continued investigation of the relationships is definitely an area of research that needs further development (Petridis et al. 2014). In a recent paper, the authors (Petridis et al. 2014) examined the nano-scale structure of a model interface by depositing films of SOM compounds of contrasting chemical character, hydrophilic glucose and amphiphilic stearic acid, onto the surface of an aluminum oxide (a common mineral in soils). They found that glucose molecules reside in a layer between the aluminum oxide and the stearic acid (Petridis et al. 2014). Similar studies involving different minerals, SOM compounds, and climate change relevant conditions are definitely warranted.

The idea of co-precipitation of SOM with Fe oxides was explored in a recent study (Eusterhues et al. 2011). These authors argued that, in soil and water, ferrihydrite frequently forms in the presence of DOM, and this disturbed crystal growth and gives rise to co-precipitation of SOM with ferrihydrite. To compare the fraction of OM co-precipitated with ferrihydrite with the fraction involved in adsorption onto pristine ferrihydrite surfaces, the researchers prepared samples of ferrihydrite associated with OM via adsorption and co-precipitation using a forest-floor extract or a sulfonated lignin. They used ^{13}C CPMAS nuclear magnetic resonance, Fourier transform infrared spectroscopy, and analysis of hydrolyzable neutral polysaccharides to study the ferrihydrite-OM associations. They found that, relative to the original forest-floor extract, the ferrihydrite-associated OM is enriched in polysaccharides, especially when adsorption took place. They also found that mannose and glucose are bound preferentially to ferrihydrite, while fucose, arabinose, xylose, and galactose accumulated in the supernatant. This fractionation of sugar monomers is more pronounced during co-precipitation and led to an enhanced ratio of (galactose + mannose)/(arabinose + xylose). Experiments with lignin revealed that the ferrihydrite-associated material is enriched in its aromatic components but had a lower ratio of phenolic C to aromatic C than the original lignin. A compositional difference between the adsorbed and co-precipitated lignin is obvious from a higher contribution of methoxy C in the co-precipitated material. Because co-precipitated SOM will behave differently than adsorbed SOM, a full array of studies are needed to gain information about SOM co-precipitation with soil minerals of different types and under conditions relevant to climate change.

3.3 Temperature Sensitivity

The temperature sensitivity of SOM is a key factor determining the response of the terrestrial C balance to global warming (von Lutzow and Kogel-Knabner 2009). Global climate C-cycle models predict acceleration of SOC losses to the atmosphere with warming, but the size of this feedback is poorly understood (Hopkins et al. 2012). Mainly for this reason and because the response of SOM decomposition to increasing temperature is a critical aspect of ecosystem responses to global change (Conant et al. 2011), many studies have addressed this topic over the last two to three years. However, despite intensive research, a consensus on the effect of temperature on SOM mineralization has not yet emerged (Davidson and Janssens 2006) and remains elusive (Ghee et al. 2013). A better understanding of the relationship between the rate and extent of SOM decomposition and soil temperature is required to make predictions of the impact of climate-change variables on SOM responses at different spatial and temporal scales.

Global climate change may induce accelerated SOM decomposition through increased soil temperature and other important changes, which collectively impact the C balance in soils. Soil C decomposition is sensitive to changes in temperature, and even small increases in temperature may prompt large releases of C from soils (Conant et al. 2008). The following related topics on temperature sensitivity of SOM were covered in other studies conducted over the last 3 years:

- Examination of various soil decomposition and chemical characteristics and their relationship to SOM temperature sensitivity (Haddix et al. 2011).
- Development of a new conceptual model that explicitly identifies the processes controlling soil OM availability for decomposition and allows a description of the factors regulating SOM decomposition under different circumstances (Conant et al. 2011).
- Studies of the vulnerability of soil C that is years-to-decades old, which makes up a large fraction of total soil C in forest soils globally, to warming (Hopkins, Torn and Trumbore 2012; Fissore et al. 2013), which imply that a major portion of soil C may become a source of atmospheric CO₂ under global warming in the 21st century (Li et al. 2013).
- Comparison of short-term and seasonal responses of soil respiration to a shifting thermal environment and variable substrate availability (Tucker et al. 2013).
- Studies of the relationship between the activation energy of decay of SOM and C and N stoichiometry, and how that can alter the relative availability of C and N as temperature changes (Billings and Ballantyne 2013).
- Another important concept that is insufficiently explored in current investigations of SOM responses to temperature change is the complete range of responses for how warming may change microbial resource demands, physiology, community structure, and total biomass (Billings and Ballantyne 2013).
- Investigations of the temperature sensitivities of basal respiration (partitioned into recent and older SOM sources) and of additional SOM mineralization associated with the addition of labile C to soil (priming effects) (Ghee et al. 2013).

Future research efforts should be focused on the following scientific hypotheses with the overall objective to improve our understanding on temperature sensitivity of SOM mineralization:

1. Several environmental constraints will obscure the intrinsic temperature sensitivity of substrate decomposition, causing lower observed “apparent” temperature sensitivity, and these constraints may, themselves, be sensitive to climate (Davidson and Janssens 2006). This hypothesis addresses the effects of environmental constraints on what is called “apparent vs. real” SOM temperature sensitivity. Several environmental constraints obscure the intrinsic temperature sensitivity of substrate decomposition, causing lower observed apparent temperature sensitivity (Davidson and Janssens 2006). In addition, factors controlling long-term temperature sensitivity of SOM decomposition are more complex due to the protective effect of the mineral matrix and thus remain as a central question (Wagai et al. 2013).
2. Physical separation or compartmentalization of substrates and decomposers in the soil matrix will decrease SOM sensitivity to temperature (Plante et al. 2009). In this study, the authors reported that the overall CO₂ efflux increased with temperature, but responses among physical protection treatments were not consistently different. Because the hypothesized attenuation of temperature sensitivity was not detected in this study, these authors concluded that, although compartmentalization of substrates and decomposers is known to reduce the decomposability of SOM labile pool, the sensitivity is probably driven by the thermodynamics of biochemical reactions as expressed by Arrhenius-type equations (Plante et al. 2009). Additional studies are needed to investigate the effects of physical separation of substrates and decomposers on SOM sensitivity to temperature.
3. The temperature response of the processes that control substrate availability, depolymerization, microbial efficiency, and enzyme production will be important in determining the fate of SOM in a warmer world (Conant et al. 2011). For a wide range of forest soils, the supply of labile substrate, controlled through extended incubation and glucose additions, exerted a strong influence on the magnitude of SOC decomposition in response to warming and showed that substrate supply can play a strong role in determining the temperature response of decomposing SOC (Fissore, Giardina and Kolka 2013). Fissore and others (2013) concluded that, because substrate supply was likely to vary both spatially and temporally, these findings have important implications for SOC processing in natural systems.
4. The temperature sensitivity will differ between freshly added organic matter and bulk soil C. The addition of fresh organic matter will stimulate the decomposition of SOM and this priming effect would be temperature dependent (Thiessen et al. 2013). The results presented in this recent study (Thiessen et al. 2013) disagreed with the view of a simple physico-chemically derived substrate-temperature sensitivity relationship of decomposition and the authors concluded that an explicit consideration of microbial processes, such as growth and priming effects, is required to address the issues raised above.

Other unresolved issues, based on the current literature, formulated as hypotheses that should be tested in future studies are:

1. *The labile pool will be more sensitive and responsive to global climate change than the recalcitrant pool.* Contradictory results are presented in the current literature from a variety of studies conducted to answer the question which SOM pool, the labile or the recalcitrant pool, is more sensitive to increasing temperatures, and whether or not the mineralization response to temperature depends on SOM mineralization rate. As soil microflora are considered to be “functionally omnipotent” (i.e, able to decompose any SOM compounds), the temperature dependence of stable SOM pools is the central issue that determines C stocks and stock changes under global warming (von Lutzow and Kogel-

Knabner 2009). The impacts of climate warming on decomposition dynamics have not been resolved due to apparently contradictory results from field and lab experiments, most of which have focused on labile C with short turnover time although the majority of total soil C stocks are comprised of OC with turnover times of decades to centuries (Conant et al. 2011). The temperature sensitivity of labile SOM decomposition could either be greater than, less than, or equivalent to that of resistant SOM (Conant et al. 2008). The initial assumption was that soil labile C was more sensitive to temperature variation, whereas SOM resistant components were insensitive and unresponsive to increasing temperature and global warming. However, kinetic theory based on chemical reactions suggests that older, more-resistant C pools may be more temperature sensitive (Conant et al. 2008). Studies have shown that the temperature sensitivity for resistant SOM pools was not significantly different from that of the labile SOM, and some authors believe that both these pools will respond similarly to global warming (Fang et al. 2005). The results of another study suggested that the temperature sensitivity of resistant SOM pools was greater than that for labile SOM and that global change-driven soil C losses may be greater than previously estimated (Conant et al. 2008). Finally, the results of a long-term study conducted with soils from across Europe demonstrated that temperature response was greater in those organic compounds that have a greater mineralization rate (i.e., stable SOM had a higher temperature sensitivity than the labile SOM) (Lefevre et al. 2014). Because of the contradictory results, additional studies are needed to address the issue of whether the mineralization response to temperature depends on the SOC mineralization rate under different soil and climate-change conditions.

2. *Because SOM is a complex mixture of different organic compounds, each of these compounds will exhibit distinct temperature sensitivity making the overall SOM response variable and time-dependent.* Much of the work conducted so far is based on an implicit assumption that soil C pools are composed of organic matter pools with uniform temperature sensitivities (Conant et al. 2008). However, as it is clearly presented above, SOM is a complex mixture of different organic compounds, each exhibiting, potentially, distinct temperature sensitivity. Unraveling the feedback to climate change is particularly difficult because diverse soil organic compounds exhibit a wide range of kinetic properties, which determine the intrinsic temperature sensitivity of their decomposition (Davidson and Janssens 2006). The question then is about uniform vs. non-uniform temperature sensitivities, and there is a need to focus research on controls over temperature sensitive SOM stabilization and destabilization processes of individual components (i.e., organic compounds) as a basis for understanding kinetic properties of key chemical reactions that determine SOM pool sizes and turnover rates. A recent laboratory incubation study of forest SOM and fresh litter material combined with nuclear magnetic resonance spectroscopy measurements was conducted to make the connection between SOM chemical composition and temperature sensitivity (Erhagen et al. 2013). The results indicated that temperature response of the fresh litter was directly related to the chemical composition of the constituent organic matter, and it decreased with increasing proportions of aromatic and O-aromatic compounds and increased with increased contents of alkyl- and O-alkyl carbons. A more detailed characterization of the ¹³C aromatic region revealed considerable differences in the aromatic region between litter and SOM, suggesting that the temperature response of decomposition differed between litter and SOM, and that the temperature response of soil decomposition processes can thus be described by the chemical composition of its constituent organic matter (Erhagen et al. 2013).
3. *Other factors (such as soil moisture content, sampling method, incubation time) and their interactions will be influential in controlling temperature response of SOM decomposition.* Temperature and moisture are primary environmental drivers of SOM decomposition, and an

improved understanding of how they interact is needed (Gabriel and Kellman 2014). Another study reported that SOM decomposition or soil basal respiration rate is significantly affected by changes in SOM components associated with soil depth, sampling method, and incubation time (Fang et al. 2005).

4.0 References

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