

DISSERTATION

A MECHANISTIC APPROACH TO MODELING SATURATION AND
PROTECTION MECHANISMS OF SOIL ORGANIC MATTER

Submitted by

Gabriel Peter Olchin

Department of Soil & Crop Sciences

In partial fulfillment of the requirements

For the Degree of Doctor of Philosophy

Colorado State University

Fort Collins, Colorado

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Committee on Graduate Work



Stephen Ogle



William Parton



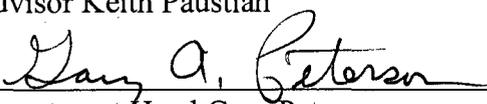
Eugene Kelly



Johan Six



Advisor Keith Paustian



Department Head Gary Peterson

ABSTRACT OF DISSERTATION
A MECHANISTIC APPROACH TO MODELING SATURATION AND
PROTECTION MECHANISMS OF SOIL ORGANIC MATTER

Simulation models have been used extensively as a research tool in the field of soil organic matter (SOM) dynamics and should embody our best understandings of the processes and mechanisms controlling these dynamics. Our objective was to develop and evaluate a SOM model based upon measureable soil organic carbon (SOC) fractions and optimize it against long-term tillage experiments in North America. This model will include (1) soil aggregate dynamics, with direct influence from tillage events; (2); and the mechanisms of SOM stabilization; and (3) explicitly address the concept of potential SOC saturation. The major proposed mechanisms for SOM stabilization – physical occlusion, organic recalcitrance, and organo-mineral interactions – have limited explicit inclusion in current SOM models.

The enhanced soil structure and higher SOC stocks measured under no-till (NT) management have been well documented. However, the roles of residue addition vs. aggregate disruption (i.e. tillage events) have not been compared at different depth increments. Pre-requisite to the major SOM stabilization mechanisms are the availability and continual addition of residues. Therefore, uniformly ^{13}C -labeled wheat residues were added to incubation cores representing soils under NT and tillage management (TM) during a yearlong *in situ* incubation at a dryland agriculture experiment site. Residue was

added directly onto the surface of NT cores, while residues were incorporated into the 0-5, 5-15, and 15-30 cm depth increments of the TM cores. Overall, our results indicate that within a plow depth of 15 cm, limiting the tillage-induced disruption of aggregates has a stronger influence than residue incorporation into the profile via tillage on the efficiency of C stabilization. However, when residues are distributed to a 30 cm depth, the negative impact of aggregate disruption through tillage appears counterbalanced with similar efficiencies of C stabilization between the NT and TM practices, possibly due to slower decomposition of residues deeper in the profile.

Conventional SOM models have been defined by kinetic, rather than functional pools. Further, soil physiochemical processes (e.g. mineral surface bindings) that inhibit the breakdown of organic compounds are generally implicit in the rate constants associated with a particular pool as a rate modifying factor. SATURN, the proposed simulation model, is comprised of functional (or measureable) pools; one of the first attempts at directly 'modeling the measureable'. The model has been initially optimized for total SOC content against seven long-term (>12 years) agroecosystem experiments; containing contrasts in tillage management (a mechanism for aggregate turnover) and different in crop rotations with a SOC gradient across sites of approximately 5 – 25 g C kg⁻¹ soil. The final optimized values resulted in a root mean square error for total SOC of 1.2 g C kg⁻¹ soil across all seven sites. This analysis is limited to the total SOC content and individual pool sizes where not optimized against which limits the degree to which we can validate the internal dynamics of the model; an added benefit of measureable pool models.

The apparent disconnect between laboratory methods and computer simulation efforts poses a significant challenge; that could possibly be resolved by developing models with functional pools. Another objective is to review the evolution of functional pool modeling from a conceptual stage, to current models, and propose future areas of research as they relate to functional pool modeling. There are many proposed benefits to using models defined by functional pools, including the ability to directly validate the internal dynamics of the model (i.e. pool behavior). This class of models also shifts from process-orientated modeling to a more mechanistic approach. We aim to examine relevant and emerging research in SOC dynamics as they relate to the development of current functional pool models. Qualitative comparisons of current functional pool models are made which reveal areas of research that should be investigated to strengthen these models.

Gabriel Peter Olchin
Department of Soil & Crop Sciences
Colorado State University
Fort Collins, Colorado 80523
Fall 2009

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DEDICATION

To my parents Peggy and Robert Olchin and my fiancé Lea Jesiolowski.

*In memory and honor of
Captain Jason M. Galus, US Army 1979 – 2009*

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I NTRODUCTION

“Attempting to hoard as much organic matter as possible in the soil, like a miser hoarding gold, is not the correct answer. Its [organic matter] value lies within its dynamic nature. A soil is more productive as more organic matter is regularly destroyed and its simpler constituents made usable during the growing season. The objective should be to have a steady supply of organic matter undergoing these processes [decomposition] for the benefit of the growing crop.”

– W.A. Albrecht. ‘Soils and Man. Yearbook of Agriculture’ 1938

Soils have played an important role in our livelihood, thanks in part to processes that occur over many scales of time and space. Many of the ecosystem services (e.g. food production, clean water) recognized by the Millennium Ecosystem Assessment (2005) are dependent upon healthy and fertile soils. Throughout anthropic history, soils were utilized for a variety of these services, including production of food and mineral resources. After many years of prolonged and intensive agriculture practices, many soils have been degraded in terms of organic carbon stocks. These losses of soil organic carbon (SOC) stocks and nutrient levels were observed over 50 years ago after continuous cultivation of arable land resulted in a large (approximately half) decrease of native SOC stocks (Haas et al., 1957; Donigian et al., 1997). However, the very decomposition processes which result reduce SOC stocks are also involved with the stabilization process which lead to the preservation of organic matter in the soil matrix. Once stabilized, organic matter serves as an important reservoir of essential nutrients for plants and microbial populations.

Recently, terrestrial carbon sequestration has been identified as yet another ecosystem service soils can provide in greenhouse gas mitigation strategies (Paustian et al., 1997). With the observed depletion of native SOC stocks following intensive agriculture, a natural 'sink' for carbon sequestration efforts potentially exists in cultivated land, given appropriate management strategies including reduced or no-tillage. Interestingly, restoration of these depleted stocks has multiple benefits, including soil carbon sequestration (both short- and long-term), increased soil fertility and higher water-holding capacity. Research into the long-term dynamics of soil C stocks in response to increased C (as residue) return to the soil is an important concept to consider for

greenhouse gas mitigation options. The relationship between C inputs and long-term (near steady-state) soil C stocks has been described as linear (see Huggins et al. 1998) or curvilinear (i.e. saturation), as shown by Stewart et al. (2007). The saturation concept is defined as the point where a soil is incapable of accumulating and stabilizing more C (Six et al., 2002; West and Six, 2007).

The relationship between tillage and increased soil aggregate turnover has been well established and makes an important link between management decisions and mechanisms of SOM stabilization (see Six et al., 1999). Their research showed that the longer turnover times of macroaggregates ($>250\ \mu\text{m}$), in the absence of tillage, promoted the formation of more stable microaggregates ($<53\ \mu\text{m}$) within the macroaggregates. The microaggregates (with longer turnover times) provide long-term protection of organic matter through organo-mineral interactions. However, this aggregate turnover model is dependent upon residue incorporation, often achieved during deep tillage events. Thus, one of our objectives was to evaluate tillage-induced influences on aggregate structure, residue-derived C stabilization, and the subsequent efficiency of C stabilization in aggregates of contrasting tillage management practices at different depth increments of the soil profile.

In an effort to monitor and describe soil organic matter (SOM) dynamics, mathematical simulation models have been widely applied to simulate the sensitivity of SOM to environmental conditions and/or management decisions. Given that SOM is subject to a wide variety of complex decomposition and stabilization processes; our best understanding of these processes is important if soil carbon sequestration is going to be considered a viable greenhouse gas mitigation option. Substantial amounts of research

has been done to investigate how climate change, management options (tillage vs. reduced- or no-tillage), crop rotations, etc. may affect carbon cycling in agroecosystems. A notable portion of this research relies, in part, on mathematical simulation models to predict the consequences of management options and variations in environmental factors, as well as to test current theory and hypotheses about decomposition processes and stabilization mechanisms of soil organic carbon (SOC) and soil ecosystem functioning (Breland, 1997). Appropriate questions then arise of how to best design and implement these models.

One of the problems with modeling SOM turnover is that it has not been possible to match conceptual, kinetically-defined pools with measurable fractions – the challenge of modeling the measurable or measuring the modelable (Elliott et al., 1996). Conventional SOM simulation models are made up of pools that are defined by their unique kinetics, rather than a specific (measurable) fraction of SOM. Others then called for SOM models that would incorporate measurable fractions rather than conceptual pools (Arah and Gaunt, 2001). The SATURN model, proposed herein, represents one of the first attempts at developing a simulation model which has internal pools that directly align with measurable SOC fractions. This model explicitly includes our current understandings of the mechanisms of SOC stabilization – physical protection, chemical recalcitrance, and organo-mineral interaction (Sollins et al. 1996). Further, the model draws inspiration from current conceptual models of soil aggregate dynamics (Six et al., 2002); a mechanism for physical protection of SOM that is sensitive to tillage management. The coupling of soil mass (i.e. aggregates) with SOC fractions was

necessary because the model pools are defined by physically derived fractions of the soil; which posed a significant challenge in the development of this model.

The scope of these collected works includes the development and initial evaluation of a SOM model defined by functional pools. The first chapter reports published results from a field incubation study which investigated the role of tillage and the effect of depth on SOM stabilization (Olchin et al., 2008). The next two chapters include the conceptualization, development and evaluation of the proposed SOM model. The final chapter presents (in review form) a current synopsis of functional pool modeling, research that motivated those efforts, and future challenges for this exciting and emerging field.

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C H A P T E R O N E

Residue Carbon Stabilization in Soil Aggregates of No-Tillage and Tillage Management of Dryland Cropping Systems

(Modified from: Olchin, G. P., S. Ogle, S. D. Frey, T. R. Filley, K. Paustian, and J. Six. 2008. Residue Carbon Stabilization in Soil Aggregates of No-Tillage and Tillage Management of Dryland Cropping Systems. Soil Sci Soc Amer J 72: 507-513)

“When soil is your muse, inspiration is only a few steps away...”

– J. Richards, The ONION

Abstract

Tillage events have an important influence on residue incorporation into soil profiles and soil aggregate disruption, and ultimately influence the net C gain or loss in soils. Thus, our objective was to evaluate tillage-induced influences on aggregate structure, residue-derived C stabilization, and the subsequent efficiency of C stabilization in aggregates of no-till (NT) and tillage management (TM) practices at different depth increments of the soil profile. Uniformly ^{13}C -labeled wheat residues were added to incubation cores representing soils under NT and TM during a year-long in situ incubation at a dryland agriculture experiment site. Residue was added directly onto the surface of NT cores, while residues were incorporated into the 0- to 5-, 5- to 15-, and 15- to 30-cm depth increments of the TM cores. We found that residue additions did not have a significant effect ($P > 0.05$) on aggregate dynamics in either NT or TM, but NT management did result in the greatest stabilization of residue-derived C (11.2 ± 2.4 g residue C kg^{-1} soil kg^{-1} residue C added, $P < 0.05$) in the macroaggregate ($> 250 \mu\text{m}$) fraction of the 0- to 15-cm increment. Residue-derived C stabilization was significantly greater ($P < 0.05$) in the 0- to 30-cm increment than in the 0- to 15-cm increment of the TM management cores. Overall, our results indicate that, within a plow depth of 15 cm, limiting the tillage-induced disruption of aggregates has a stronger influence on the efficiency of C stabilization than residue incorporation into the profile via tillage. When residues are distributed to a 30-cm depth, however, the negative impact of aggregate disruption through tillage appears counterbalanced, with similar efficiencies of C stabilization between the NT and TM practices, possibly due to slower decomposition of residues deeper in the profile.

Introduction

No-till (NT) management can increase soil organic C (SOC) levels (Lal and Kimble, 1997; Paustian et al., 2000). This is an important management decision because terrestrial C sequestration has been suggested as a potential strategy for greenhouse gas mitigation (Council for Agriculture Science and Technology, 2004, p. 120). Terrestrial C sequestration is achieved through SOC stabilization by physical occlusion within aggregates (Tisdall and Oades, 1982; Elliott, 1986; Six et al., 2000b), chemical interactions with clay minerals (Sørensen, 1972; Christensen, 1996; Hassink, 1997), and biochemical recalcitrance (Leavitt et al., 1996; Krull et al., 2003). These three mechanisms are influenced in part by the spatial variance of soil properties and C inputs (e.g., residue additions or root exudates) to the soil, as well as management decisions.

The manner by which crop residues are introduced to the soil matrix differs dramatically between NT and tillage management (TM). Under NT management, crop residues are left on the surface of the soil after harvest, whereas residues are mechanically incorporated into the soil during tillage. Stable isotopes have shown that the majority of C from corn residues is concentrated in the upper 5 cm under NT management, but a more uniform vertical distribution throughout the plow depth is achieved during tillage (Balesdent et al., 1990; Angers et al., 1995).

Recently decomposed crop residues and soil organic matter (SOM) are central to the aggregate hierarchy model of Tisdall and Oades (1982). They proposed that transient forms of SOM could act as binding agents, causing microaggregates (53–250 μm) to form stable macroaggregates ($>250 \mu\text{m}$). Furthermore, Puget et al. (1995) proposed that recently introduced crop residues are preferentially incorporated into aggregates, aiding

in soil stability. Similarly, Six et al. (1999) suggested that the addition of new residues in NT management promote organic matter stabilization through the binding of primary soil particles and old microaggregates into new macroaggregates. Fragmented crop residues (i.e., particulate organic matter [POM]) can form the nuclei for new microaggregates that can be bound together by transient, labile organic matter to form new macroaggregates, or new microaggregates may form within the larger macroaggregates around POM (Golchin et al., 1994; Six et al., 1998). Several studies have shown that incorporation of residue-derived C into aggregates increased with increasing aggregate size (Jastrow et al., 1996; Six et al., 2000b; Puget and Drinkwater, 2001). Consequently, macroaggregate formation could be enhanced by residue additions throughout the entire plow layer with TM. In contrast, under NT management, residues are concentrated near the soil surface so that a smaller soil volume is exposed to fresh residues, which may limit new aggregate formation.

Tillage has a strong influence on soil aggregation and SOM dynamics by increasing macroaggregate turnover and reducing microaggregate formation compared with NT (Six et al., 1999). The disruption of aggregates releases physically protected POM, increasing its susceptibility to decomposition (Jastrow and Miller, 1997). In addition, intra-aggregate POM is less susceptible to decomposition relative to free POM in the soil matrix (Besnard et al., 1996; Six et al., 1999) due in part to the physical and chemical protection that aggregates provide. Tillage also enhances the decomposition of total SOC, however, by mixing plant residues with soil (Holland and Coleman, 1987), disrupting aggregates (Beare et al., 1994a), and enhancing dry-wet and freeze-thaw cycles (Balesdent et al., 2000). Consequently, physical disturbances resulting from tillage

and other environmental phenomena may destabilize macroaggregates, thereby offsetting some or all of the organic matter stabilization potential from macroaggregate formation. Thus, the stabilization of SOM may be enhanced in NT management because macroaggregates that are formed are less susceptible to disruption from tillage-induced physical disturbances.

Our objectives were to (i) investigate the influence of residue incorporation on aggregate formation, (ii) evaluate the stabilization of residue-derived C in aggregate fractions between NT and TM of dryland cropping systems, and (iii) evaluate the efficiency of C stabilization between NT and TM. Here we have defined efficiency of C stabilization as the percentage of residue-derived C that is associated with soil aggregate fractions at the end of a given time frame (e.g., 1 yr in our study). Quantifying residue-derived C stabilization between contrasting tillage management practices allowed us to determine the relative importance of residue addition vs. aggregate disruption at different depths in the profile, and consider the consequences for C sequestration.

Methods and Materials

Study Site and Experiment Design

This field incubation study took place at the Sustainable Dryland Agroecosystem Management Project located in Sterling, CO (40°22'12" N, 103°7'48" W). The soil is a fine-silty, mixed, mesic Aridic Argiustoll (Peterson et al., 1993). At the start of the experiment, 32 stainless steel incubation cores (9.0-cm diam.) were installed in the summit position of a NT, wheat (*Triticum aestivum* L.)–corn (*Zea mays* L.)–fallow rotation (under fallow during the incubation) established in 1985. Cores were arranged in

four randomized blocks. Within each block there were eight cores representing TM and an additional eight cores for NT. Four TM and NT cores were amended with ^{13}C -labeled residues. Each treatment core had a corresponding control core with no residue added to evaluate a change in the isotopic signature relative to the background SOM during the incubation period (1 yr). Each amended core and corresponding control was randomly placed within the block, ensuring at least 50 cm between individual cores.

Labeled wheat enriched in ^{13}C ($\delta^{13}\text{C} = 797.55\text{‰}$) was grown to maturity within a closed growth chamber with continuous labeling of $^{13}\text{CO}_2$. The labeled wheat residue was cut into 1- to 2-cm pieces and added to a closed system (i.e., an incubation core) at the Sterling site, with a soil having a contrasting background $\delta^{13}\text{C}$ signature ($\delta^{13}\text{C} = -17.7\text{‰}$) a similar approach to the methods of Aita et al. (1997).

The stainless steel cores were driven into the ground for both treatments to minimize differences in initial disturbance effects. Soil cores for the NT treatment were taken from the wheat–corn–fallow NT plot in the field experiment, whereas the soil cores for the TM treatment were transplanted from an adjacent field (same texture and summit slope position) that had previously been under long-term tillage (stubble mulch) management. Soil was removed from each core and thoroughly mixed with a hand trowel. Labeled wheat residues, 2.5, 5, and 5 g, were incorporated by hand into the 0- to 5-, 5- to 15-, and 15- to 30-cm depth increments, respectively, for the amended TM treatment cores. The soil from each depth increment was then placed in the core, gently compressed to the same volume, and moved to the study plot (NT management, fallow cover during the year of the incubation). No-till cores received 2.5 g of labeled wheat residues on the surface of the soil within the core. Thus, the NT and TM cores received

2.5 and 12.5 g of the labeled wheat residue, respectively. Residue addition rates were designed to add equal amounts of residue to the surface layer of the NT and TM treatments and similar amounts of residue per unit volume of soil across the depth increments of the TM treatment. Furthermore, more residues were added to the deeper depth increments (5–15 and 15–30 cm) of the TM cores to ensure that the ^{13}C signature would be detected. Accordingly, the focus of this study was to compare relative stabilization of residue-derived C between tillage treatments and, therefore, data were normalized on a per gram of added residue basis. The tops of all the cores were covered with aluminum mesh to minimize losses of residue or contamination from outside sources. Aluminum mesh was also placed over control cores to minimize differences.

Soil Sampling

Two randomly selected pairs of amended and unamended cores for NT and TM were collected from each block at the start of the experiment (July 2004), immediately after residue addition. Initial incubation cores were collected to determine the baseline ^{13}C content of the soil and to measure any contamination effects of adding fresh residues on the different SOC fractions. Final samples were collected (July 2005) after 1 yr of incubation under field conditions at the Sterling, CO, site. Soil cores remained intact and cool during transportation to the laboratory and were refrigerated for a maximum of 1 to 2 d before initial preparation. Intact soil cores were weighed and subsamples taken for moisture analysis. No-till incubation cores were then divided into two depth increments (0–5 and 5–15 cm) for lab analysis, while the TM cores had an additional 15- to 30-cm increment.

Field-moist soils were then gently passed through an 8-mm sieve, removing large rocks, recognizable surface litter, residues >8 mm, and root material. The remaining soil was then air dried and stored at room temperature. Bulk density was calculated based on the soil mass and core volume after adjusting for the moisture content estimated from drying a subsample at 105 °C for 24 h.

Aggregate Soil Organic Matter Fractionation

The physical fractionation (Fig. 1.1) of air-dried, whole soil subsamples was accomplished through wet sieving (Elliott, 1986) and further fractionation using a microaggregate isolator (Six et al., 2000a). For wet sieving, a 100-g subsample was subjected to a slaking period of 5 min in deionized water. Floating material, considered the free light fraction, was aspirated from the surface and transferred to an aluminum pan during the slaking process. Samples were manually wet sieved on 250- and 53- μm sieves with 50 vertical, 3-cm strokes in a 2-min period. Macroaggregates were collected from the 250- μm sieve and free microaggregates from the 53- μm sieve by backwashing the material into aluminum pans. Material <53 μm , which is the silt plus clay fraction, was centrifuged and the pellet transferred to an aluminum pan. All isolated fractions were dried at 60 °C in a forced air oven. Mass yield after fractionation was $97.4 \pm 1.1\%$ (mean \pm standard deviation) (data not shown).

A 10-g subsample of the macroaggregates was then further fractionated with the microaggregate isolator (Six et al., 2000a). The isolator gently dispersed the macroaggregate subsample using 50 glass beads (4-mm diam.) under a continuous flow of deionized water. Microaggregates and silt- and clay-sized particles were flushed

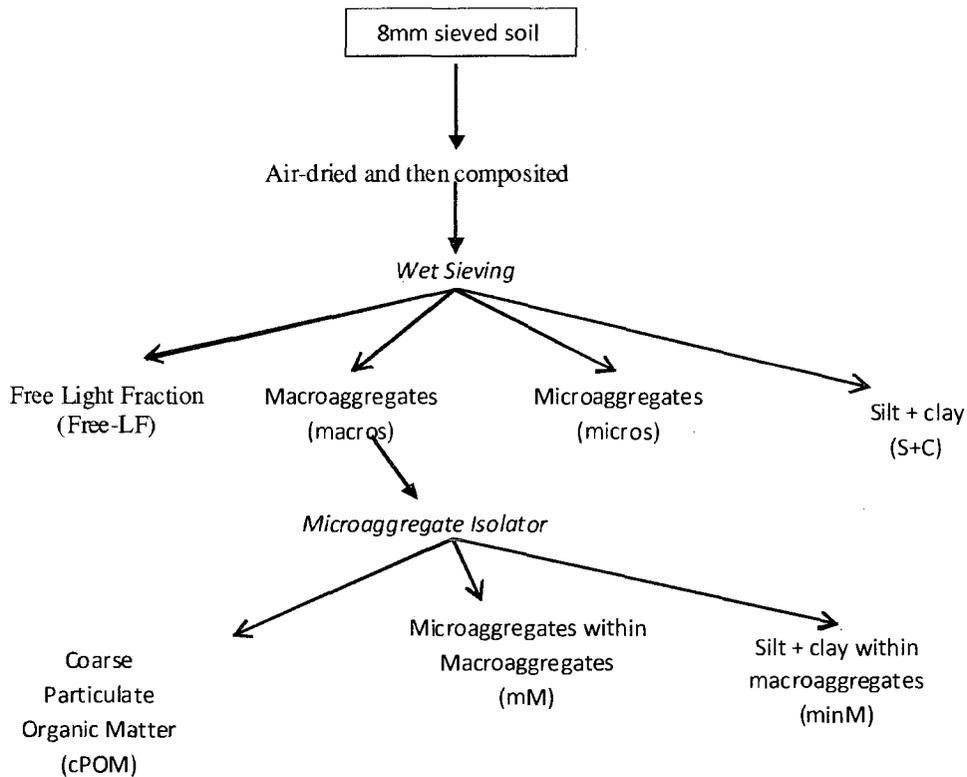


Figure 1.1 Fractionation scheme for the isolation of aggregate size classes by wet sieving and macroaggregate disruption (Six et al., 2000a).

through the 250- μm mesh screen as the macroaggregates were disrupted. Three fractions were collected: (i) $\geq 250\text{-}\mu\text{m}$ coarse particulate organic matter (cPOM), (ii) 53- to 250- μm microaggregate-sized fraction within macroaggregates (mM), and (iii) $< 53\text{-}\mu\text{m}$ silt plus clay within macroaggregates (minM). Mass yield after macroaggregate fractionation was $98.6 \pm 2.4\%$ (mean \pm standard deviation; data not shown).

Carbon and Isotopic Analyses of Soil Organic Carbon Fractions

Before isotopic analysis, all fractions were pulverized and placed in a HCl fumigation chamber for 30 to 45 min to remove any inorganic C in the form of $\text{CaMg}(\text{CO}_3)_2$ or CaCO_3 (Harris et al., 2001). Note that the larger residues and the free light fraction were not analyzed because they are not considered part of the SOM. Organic C content and isotopic analysis for all fractions were measured using a Carlo Erba NA 1500 CN Analyzer (Carlo Erba, Milan, Italy) coupled to a GV Isochrom mass spectrometer (GV Instruments, Manchester, UK). Organic C recovery was $98.2 \pm 6.6\%$ (mean \pm standard deviation) and $95.7 \pm 7.1\%$ for the wet-sieving and microaggregate isolation procedures, respectively (data not shown). Results were expressed as:

$$\delta^{13}\text{C}\text{‰} = \left[\frac{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{sample}} - \left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{reference}}}{\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{reference}}} \right] 1000 \quad (1)$$

where $\left(\frac{^{13}\text{C}}{^{12}\text{C}} \right)_{\text{reference}}$ is the international Pee Dee Belemnite standard. The proportion of C derived from the wheat residue was calculated according to a simple mixing model (Cerri et al., 1985):

$$f = \frac{\delta^{13}\text{C}_1 - \delta^{13}\text{C}_S}{\delta^{13}\text{C}_1 - \delta^{13}\text{C}_R} \quad (2)$$

where $\delta^{13}\text{C}_I$ is the isotopic ratio of the soil at the beginning of the experiment, $\delta^{13}\text{C}_S$ is the isotopic ratio of the soil or aggregate sample after the incubation, and $\delta^{13}\text{C}_R$ is the isotopic ratio of the labeled residue. The incorporation value, f , is the proportion of residue-derived C present in the physically isolated fractions or whole soil. Residue-derived C concentrations for the individual fractions are a product of the incorporation value and the C concentration (g C kg^{-1} soil) for each sample. Total residue-derived C stabilization stocks (on a whole-soil basis) were calculated as a function of f , bulk SOC concentration, depth increment, and soil bulk density.

Statistical Analysis

Data were analyzed using ANOVA with main effects for depth (0–5, 5–15, and 15–30 cm), treatment (TM or NT), and aggregate fraction (SAS Institute, Cary, NC). We specifically compared the initial and final samples to account for differences in the initial conditions between the tilled field and the NT experimental plot. Separate analyses were conducted for the fractions derived from wet sieving (macroaggregates, microaggregates, and silt plus clay) and the fractions isolated from the macroaggregates (cPOM, mM, and minM). Analyses were conducted for residue-derived C stabilization and relative mass distributions of the aggregate size classes. Due to the unbalanced design of depth increments in this experiment, analyses comparing the two tillage treatments included only the first two depths. A separate analysis was conducted evaluating differences across the three depths in the TM treatment. Pairwise comparisons were made using the Bonferroni method with an $\alpha = 0.05$.

Results and Discussion

Soil Structure and Influence of Residue Incorporation

At the onset of the incubation, there were significantly more macroaggregates under NT for the 0- to 5-cm layer compared with the tillage treatment (Fig. 1.2). This result is consistent with previous findings demonstrating that the transient binding agents of macroaggregates are disrupted by tillage-induced disturbance (Elliott, 1986; Besnard et al., 1996; Six et al., 2000b).

The proportion of macroaggregates did not increase during the incubation under the NT treatment, where aggregate dynamics may have reached steady state during the long-term (20-yr) continuous NT management at the experiment site. The aggregate proportions of the tillage treatment converged with the proportions measured under NT following 1 yr of field incubation without further tillage events (Fig. 1.2). These findings are similar to an analogous incubation experiment by Coppens et al. (2006), who found that there were no significant differences in the mean weight diameter of soils receiving surface-applied or incorporated (over a 10-cm depth) residues after a 33-wk laboratory incubation with labeled residues.

Though not significant, the macroaggregate and minM fractions showed increases in the tillage treatment (0–5 cm) corresponding with decreases in free microaggregates, which is consistent with the aggregate hierarchy model of Tisdall and Oades (1982). Final aggregate proportions for both TM and NT decreased in the following order for the upper two depths (0–5 and 5–15 cm): microaggregates > silt plus clay \approx macroaggregates. Within the macroaggregates, the proportions decreased from mM \approx cPOM > minM. The binding of primary particles into microaggregates by persistent

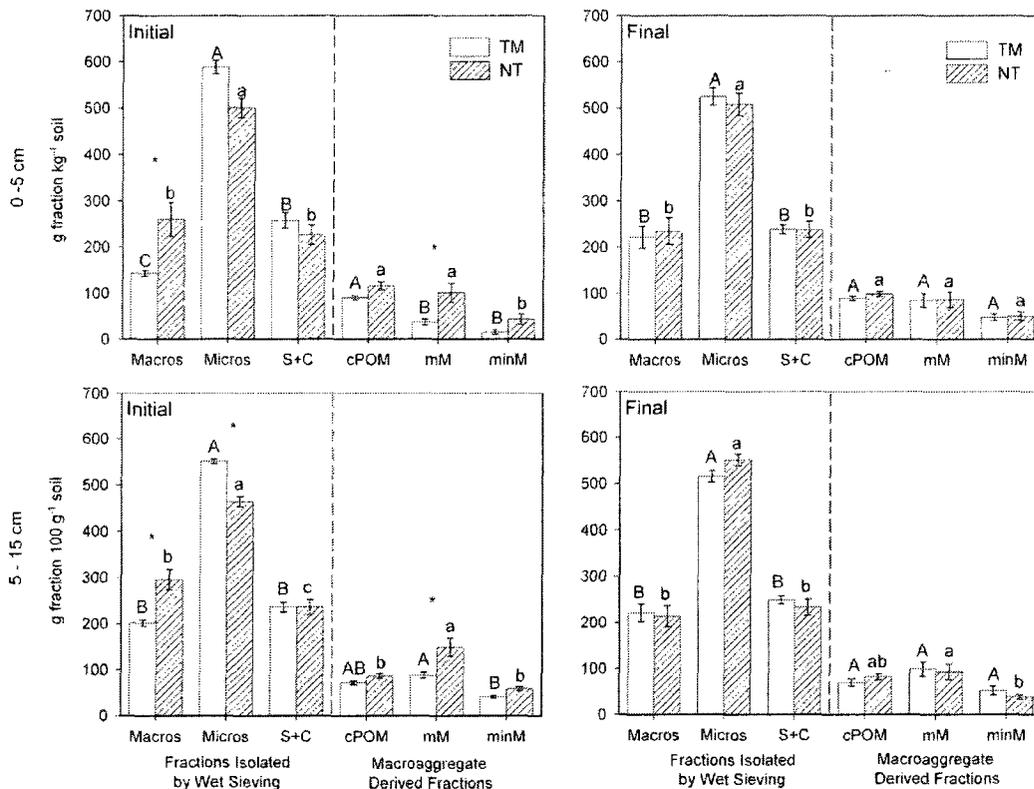


Figure 1.2. Initial and final aggregate distributions for the first two depths (0-5 cm, and 5-15 cm) of the tillage management (TM) and no-tillage (NT) treatments at Sterling, CO. The macroaggregate (macros), microaggregate (micros), silt + clay (S+C), coarse particulate organic matter (cPOM), microaggregates within macroaggregates (mM), and silt + clay within macroaggregates (minM) fractions are expressed in terms of g kg^{-1} whole soil. Error bars represent \pm one standard error of the mean. Different letters represent significant differences (Bonferroni's Adjustment; $\alpha = 0.05$) within each sieving class among tillage treatment and depth increment. An (*) denotes significant differences between the two tillage treatments within each aggregate class and depth combination. Uppercase and lowercase letters correspond to the TM and NT treatments, respectively.

organic matter, in addition to macroaggregate turnover, could explain why free microaggregates (53–250 μm) dominate the aggregate distributions in each treatment and depth increment because microaggregates are inherently more stable than macroaggregates. Few significant differences were measured among the macroaggregate-derived fractions within a tillage treatment and also for comparisons between tillage treatments (Fig. 1.2).

Differences in aggregate class distributions after 1 yr of field incubation were measured when comparing across the three depth increments of the TM treatment. Significant statistical differences occurred among fractions (within a given depth increment) and among depth increments for a given fraction (Fig. 1.3). Microaggregates consistently dominated the aggregate distributions, as observed in other experiments with similar slaking treatments and textures that varied from sandy loam to silty clay loam (Cambardella and Elliott, 1993; Jastrow et al., 1996; Six et al., 2000b). In the deepest increment (15–30 cm) of the tillage treatment, there were significantly more macroaggregates and fewer microaggregates compared with the upper two increments (Fig. 1.3). Presumably, the reduction of free microaggregates was a result of new macroaggregate formation, as confirmed by the significantly greater proportion of mM and minM in the 15- to 30-cm increment. Across depth increments, the proportions of mM and minM within macroaggregates increased while the proportion of cPOM decreased. This suggests that new macroaggregates were formed in the deepest increment from the binding of microaggregates with transient organic matter from decomposition processes of cPOM.

We also evaluated the direct effects of residue addition on aggregate dynamics relative to the unamended cores. These comparisons revealed no significant ($P > 0.05$) differences among aggregate distributions between the control and amended cores for either tillage treatment (data not shown). This suggests that binding agents from the decomposition of incorporated residues are not an important mechanism for macroaggregate formation in the semiarid environment of our field incubation during an annual cycle. Prior research has suggested, however, that the decomposition of organic

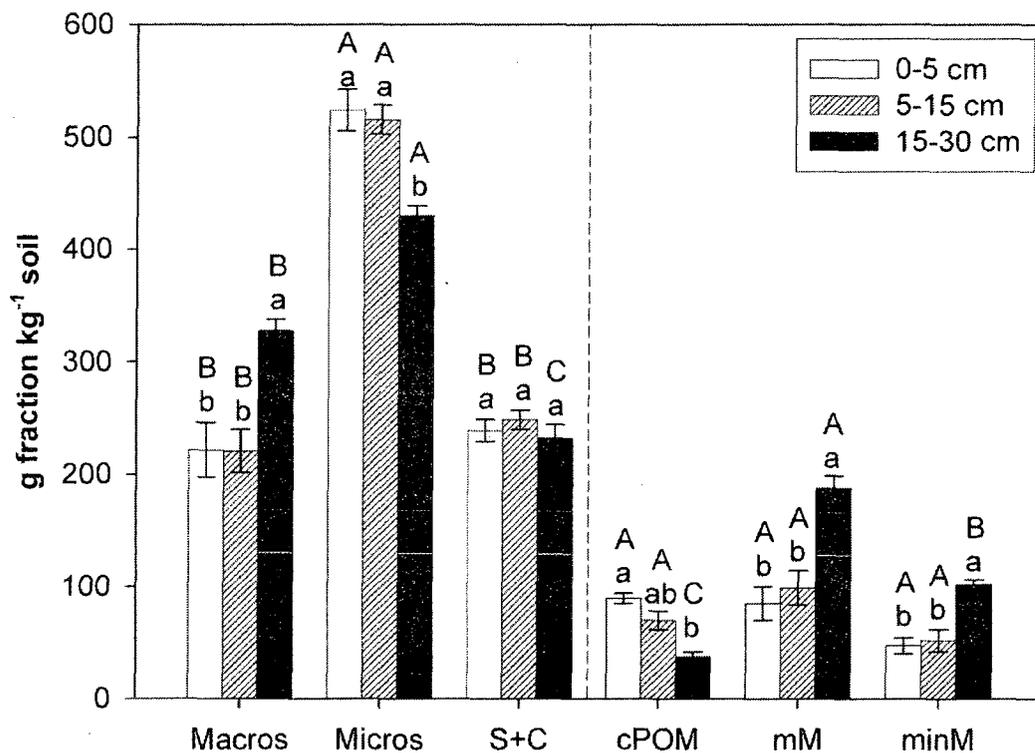


Figure 1.3. Final aggregate distributions for the tillage management (TM) treatment for each depth increment (0-5 cm, 5-15 cm, and 15-30 cm). The macroaggregate (macros), microaggregate (micros), silt + clay (S+C), coarse particulate organic matter (cPOM), microaggregates within macroaggregates (mM), and silt +clay within macroaggregates (minM) fractions are expressed in terms of g kg^{-1} whole soil. Error bars represent \pm one standard error of the mean. Aggregate proportions followed by a different uppercase letter within the depth increment/isolation method are significantly different; aggregate proportions followed by a different lowercase letter within an aggregate class are significantly different (Bonferroni's Adjustment; $\alpha = 0.05$).

matter provides binding agents and a nucleus for aggregate formation (Oades, 1984; Beare et al., 1994b). In shorter time frames, buried residues may induce an initial increase in microbial decomposition, increasing the formation of transient binding agents, countering the disruption of aggregates by tillage through the formation of new macroaggregates (Bossuyt et al., 2002). The aggregate distributions in our study were

analyzed during a much longer period, spanning 1 yr, where an initial increase in macroaggregate formation could not have been detected. Our incubation took place in situ at a semiarid dryland agriculture system, whereas incubations are typically conducted under laboratory conditions. The presumed lower moisture content of our soil cores, compared with laboratory conditions, during the incubation period probably hindered the decomposition of residues and macroaggregate formation, as described above.

Residue Carbon Stabilization Related to Tillage Disturbance

A significantly greater amount of residue-derived C (10.2 ± 2.2 g residue C kg⁻¹ soil kg⁻¹ residue C added, $P < 0.05$) was stabilized in the macroaggregate fraction of the NT treatment in the 0- to 5-cm increment (Fig. 1.4A). The difference in residue C stabilization in the 0- to 5-cm increment was due in part to the significantly more residue C in the cPOM fraction ($P < 0.05$, Fig. 1.4A) of the NT treatment. Additionally, fresh residues have been shown to be preferentially incorporated into larger aggregates under NT management (Cambardella and Elliott, 1993; Jastrow et al., 1996), similar to our results for the NT treatment. This result confirms the critical physical protection afforded to cPOM by macroaggregates and the differences between tillage regimes on the stabilization of SOM.

Not surprisingly, significantly ($P < 0.05$, data not shown) more C was stabilized in the aggregate fractions of the TM treatment in the 5- to 15-cm layer because litter was directly added into this layer as part of the experimental design. In contrast, litter was only placed on the surface of the NT treatment. Gale et al. (2000) also reported that

surface-applied residues play a minor role in macroaggregate formation deeper in the soil profile under NT management.

Residue-derived C stabilization in the 0- to 15-cm increment (Fig. 1.4B) was similar to stabilization in the 0- to 5-cm increment (Fig. 1.4A). More C was stabilized in a majority of the aggregate fractions under NT, with significant differences in the macroaggregate and cPOM fractions, suggesting a faster stabilization rate and greater residue stabilization efficiency under NT. It is important to note that the differences were not significant for all of the individual aggregate classes (Fig. 1.4B), but stabilization was significantly greater at the whole-soil level for the NT treatment (Table 1.1). This finding is similar to the results of Six et al. (1999), who reported that although similar concentrations of crop-derived C were initially stabilized within the macroaggregate fraction under NT and conventional tillage (i.e., TM), there were significant differences in the total amount of C stabilized under each tillage treatment.

Therefore, as originally proposed by Six et al. (1999), Fig. 1.4B demonstrates that C associated with microaggregates (both free and intra-aggregate) is subject to physical protection through inclusion in macroaggregates and that the mechanisms of C stabilization in microaggregates are similar under the NT and TM treatments.

Residue Stabilization across Depths in the Tillage Management Treatment

During tillage, surface residues are incorporated throughout the tillage profile, and consequently tillage depth substantially influences their distribution and concentration (see Allmaras et al., 1996; Etana et al., 1999). Thus, the amount of C stabilized within

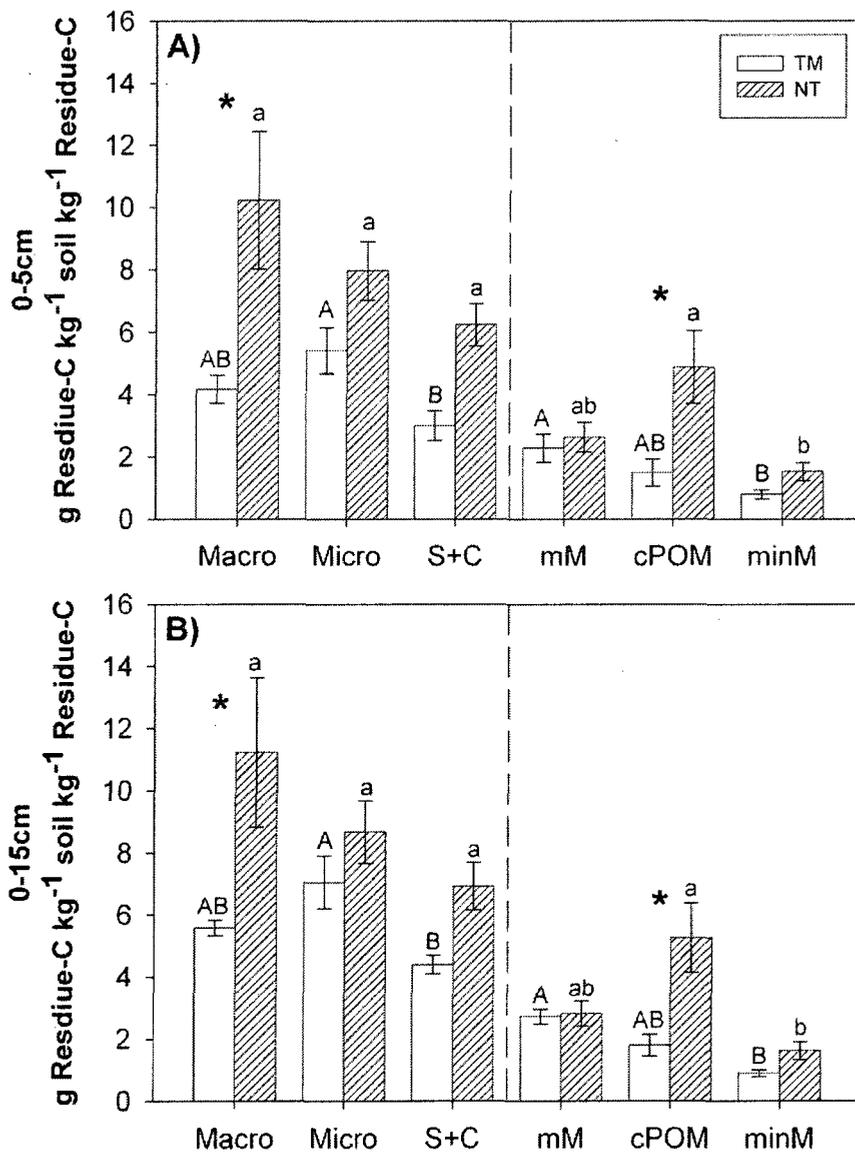


Figure 1.4. Residue-derived C stabilization for the 0-5 and 0-15 cm depth increments of the tillage (TM) and no-tillage (NT) treatments at Sterling, CO. The macroaggregate (macros), microaggregate (micros), silt +clay (S+C), coarse particulate organic matter (cPOM), microaggregates within macroaggregates (mM), and silt +clay within macroaggregates (minM) fractions are all expressed in terms of g residue-derived C kg⁻¹ soil g⁻¹ residue-derived C added. Error bars represent \pm one standard error of the mean. Different letters represent significant differences (Bonferroni's Adjustment; $\alpha = 0.05$) among each aggregate class within sieving method and tillage treatment for each depth. Uppercase and lowercase letters correspond to the TM and NT treatments, respectively. Significant differences between TM and NT within each aggregate class are shown by an (*).

Table 1.1. Stabilized residue-derived C stocks and subsequent C stabilization efficiency for the two treatments and depth increments.

Depth Increment [†]	Residue		Efficiency (%)
	Initial	Stabilized	
	-----g C m ⁻² -----		
NT			
0-15 cm	171.74	24.9 (±2.7) [‡]	14.5 (±1.6) ^{A§}
TM			
0-15 cm	515.23	52.7 (±3.9)	10.2 (±0.8) ^B
0-30 cm	858.72	105.4 (±4.5)	12.2 (±0.5) ^A

[†]NT, No-tillage; TM, Tillage management

[‡] Errors in parentheses represent ± one standard error of the mean.

[§] The capital letters represents significant differences (Student's t-test; $\alpha = 0.05$) among the efficiencies.

aggregate classes was strongly influenced by the initial amount of residue added in the TM treatment. Significantly more residue-derived C (data not shown, $P < 0.05$) was stabilized in the 15- to 30-cm increment of the TM treatment where more residues were added. We must also recognize that there was the potential for leaching of dissolved organic C into the deeper increments during the course of the field incubation, which would complicate our results. It seems unlikely, however, that a significant amount of C would be transported deeper in the profile through leaching in the semiarid dryland agricultural systems of eastern Colorado.

After normalization for the initial amount of residue added, there were no significant differences within any aggregate class between the three depth increments (Fig. 1.5). More total C was stabilized in the 0- to 30-cm depth, however, than the 0- to 15-cm depth on a whole-soil basis even after normalization (Table 1.1). The results of our aggregate distributions (data not shown) suggest that fresh residues may not be as important in aggregate dynamics in our semiarid dryland agroecosystem site; however,

there may have been less disruption of the macroaggregates at the deeper depth from nontillage events such as dry–wet and freeze–thaw cycles. As shown above, a higher proportion of macroaggregates occurred below the typical plow depth (12–15 cm), suggesting greater potential for stabilization of C by physical protection provided by macroaggregates (Fig. 1.3). Decomposition could also be limited by soil moisture and decreased temperature deeper in the profile, which could also reduce the loss of SOM deeper in the profile.

Efficiency of Residue Carbon Stabilization

Efficiency of residue-derived C stabilization is defined as the percentage of residue-derived C that is associated with soil aggregate fractions at the end of a given time frame (e.g., 1 yr in our study). Accordingly, residue-derived C stabilization was significantly ($P < 0.05$) more efficient under NT ($14.5 \pm 1.6\%$) than TM ($10.2 \pm 0.8\%$) management in the 0- to 15-cm depth, but efficiency did not differ significantly compared with TM in the 0- to 30-cm depth (Table 1.1). Thus, the efficiency of C stabilization in the tillage treatment increased by distributing residues deeper in the profile to a 30-cm depth compared with the typical plow increment (12–15 cm). When residues were distributed throughout a 30-cm depth, they were exposed to a greater volume of soil and had more potential for stabilization in soil aggregates. The simulated tillage event over 30 cm appeared to cover a depth where the C stabilization efficiency was roughly similar for the NT ($14.5 \pm 1.6\%$) and TM ($12.2 \pm 0.5\%$) treatments.

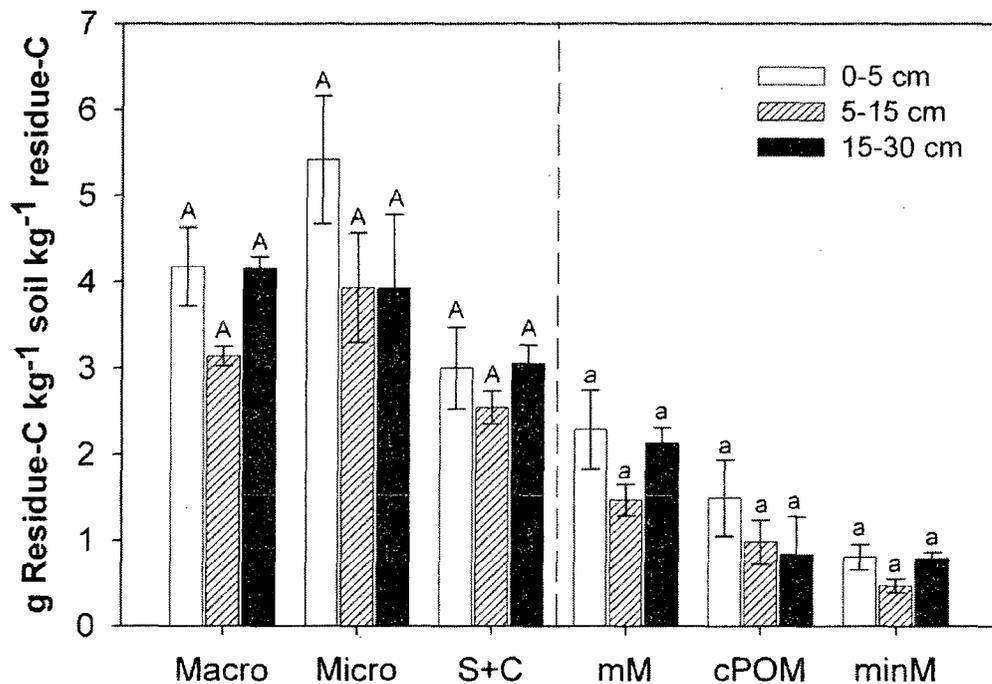


Figure 1.5. Residue-derived C stabilization across the three depths (0-5 cm, 5-15 cm, and 15-30 cm) of the tillage management (TM) treatment at Sterling, CO. The macroaggregate (macros), microaggregate (micros), silt + clay (S+C), coarse particulate organic matter (cPOM), microaggregates within macroaggregates (mM), and silt +clay within macroaggregates (minM) fractions are expressed in terms of g residue-derived C kg⁻¹ soil g⁻¹ residue-derived C added. Error bars represent \pm one standard error of the mean. Different letters represent significant differences (Bonferroni's Adjustment; $\alpha = 0.05$) between the three depths within each aggregate class. For example, there was not a comparison made between macroaggregates and microaggregates for any depth. Uppercase and lowercase letters correspond to the wet sieving and macroaggregate-derived fractions, respectively.

Conclusions

Under the proposed aggregate turnover model of Six et al. (1999), the addition of residues into the soil matrix plays an important role in new aggregate formation. Our findings from a single-year incubation in a semiarid dryland agriculture setting indicate that residue additions did not foster greater macroaggregate formation. The greatest stabilization of residue-derived C occurred, however, in the macroaggregate fraction

(>250 μm) under NT management in the 0- to 5-cm depth increment (Fig. 1.4A), confirming the model presented by Six et al. (1999) on macroaggregate dynamics and the physical protection provided by soil aggregates under NT management. Accordingly, cPOM is more sensitive to tillage management that can disrupt macroaggregates and expose the physically protected cPOM to the soil environment and decomposition. Thus, limiting the disruption of aggregates by tillage down to 15 cm has a stronger influence than residue addition on the aggregate formation and physical protection of SOM during an annual cycle.

Alternatively, when residues were incorporated into the soil to a 30-cm depth, the relative efficiency of residue-derived C stabilization of the NT treatment (0–15 cm) was not significantly different from the tilled soil at the Sterling site. This comparison suggests that if fresh residues are incorporated below a tillage depth of 15 cm through annual tillage in a semiarid, dryland agriculture setting, the negative impact of aggregate disruption through tillage may be offset by slower decomposition of residues deeper in the profile, possibly from decreased temperature and moisture availability that may limit decomposition. Thus, an annual deep tillage event followed by no additional tillage passes could potentially serve as a strategy to sequester C during a 1-yr period in semiarid dryland cropping systems. In addition, the long-term dynamics of residue-derived C stabilization below the typical plow depth may have the potential for increased soil C sequestration beyond an annual cycle, which requires further investigation. No-till also has other benefits, however, such as decreased soil erosion and improved soil water conservation, which should also be considered when making a management decision.

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C HAPTER TWO

Modeling SOM stabilization processes in agroecosystems: Model description

“Where there is light Saturn brings darkness, where there is heat Saturn brings cold, where there is joy Saturn brings sadness, where there is life Saturn brings death, where there is luck Saturn brings misfortune, where there is unity Saturn brings isolation, where there is knowledge Saturn brings fear, where there is hope Saturn brings skepticism and stalling. This isn't always a bad thing however...”

– Author Unknown

Abstract

The major proposed mechanisms for soil organic matter (SOM) stabilization – physical occlusion, organic recalcitrance, and organo-mineral interactions – have limited explicit inclusion in current SOM models. Further, soil physiochemical processes (e.g. mineral surface bindings) that inhibit the breakdown of organic compounds are generally implicit in the rate constants associated with a particular pool as a rate modifying factor. We have developed a simulation model of SOM comprised of functional, or measureable, pools; one of the first attempts at directly ‘modeling the measureable’. There is potential for many added benefits by constructing a model with measureable pools, including the direct validation of internal dynamics. The fundamental concepts of this model include potential whole soil C saturation (expressed as a non-linear relationship between clay content and soil organic C) and aggregate turnover; with external influences from disturbances (e.g. tillage events), climate, and pedon characteristics. We have defined nine state variables which are broadly categorized into ‘aggregated’ and ‘non-aggregated’ pools. Here we explore the development of the model and introduce qualitative assessments of model performance. We propose a plausible fractionation scheme by combining common methods that ultimately isolates the fractions in the model. Some pools within the model behave in a linear fashion to increased C inputs, while others have the potential for saturation; demonstrated by an asymptotic relationship to increased C inputs. Initial evaluations of model performance show that tillage results in a shift of aggregate-associated C to the non-aggregated fractions.

Introduction

The persistence of organic matter in soil is attributed to three main phenomena: 1) the inherent recalcitrance of different organic compounds; 2) the physical occlusion within soil particles which limits decay processes; and 3) the organo-mineral interactions that inhibit enzymatic attack (Sollins et al., 1996; Baldock et al., 2004). While these mechanisms have been articulated in conceptual models of soil organic matter (SOM) dynamics (Six et al., 2002; von Lützow et al., 2008), they have generally not been represented in explicit terms within process-based models of SOM dynamics.

Variation in the decay rate of soil organic substances is represented in process-based models either as discrete pools with different specific decay rates or by representing the specific decay rate as a function of a continuous 'quality' densities (see reviews by Paustian, 1994; McGill, 1996; Falloon and Smith, 2000). A key assumption is that as fresh organic matter (litter) is decomposed there is a preservation of more recalcitrant primary compounds and/or a recombination of partially decomposed residues into more recalcitrant organic compounds giving rise to progressively longer residence times for pools 'lower' in the catenary sequence (*sensu* Swift et al., 1979), or a progressive deterioration in the quality of a litter cohort in the case of the continuous quality functions (e.g. Bosatta and Agren, 1985, 1991). These representations largely reflect the perceived role of the inherent recalcitrance of organic compounds, either as primary organic compounds (i.e. lignin) or as secondary organic compounds, in determining the rates of SOM turnover.

In most current models, soil physiochemical processes (e.g. mineral surface bindings, occlusion) that inhibit the breakdown of organic compounds are generally implied in the decomposition rate constants as a rate modifying factor, for example, soil texture (see Parton et al., 1987). The thought being that as clay content increases decomposition rate constants are slowed down according to an empirical function. Early models had SOM pools that included the concept of physical protection, but the mechanisms were not directly expressed; rather, the 'protected' pools simply had slower specific decay rates – an implied effect of physical protection (van Veen and Paul, 1981; Verberne et al., 1990). The association of SOM with clay mineral surfaces has been the main mechanism for physical protection articulated in models and soil clay content has been used as a rate modifier in many SOM models (e.g. Jenkinson and Rayner, 1977; Parton et al., 1987). However, more specific attributes of the mineral surfaces involved in stabilizing SOM, such as their total surface area, have generally not been introduced into models.

Finally, the mechanism of physical occlusion of organic matter within soil aggregates – reducing decomposition via reduced oxygen supply, and pore size restrictions for soil biota – has generally not been explicitly represented in SOM models. This mechanism implies a representation of transient soil aggregate dynamics, involving the formation and subsequent breakup of organic matter and mineral assemblages and the role of physical disturbance in influencing aggregate dynamics. Recent models of aggregate turnover (e.g. De Gryze et al., 2006) have begun to explore these issues but they are limited in the treatment of SOM at the whole soil level.

Regardless of which mechanisms are included as decay rate modifiers, SOM simulation models generally employ first-order kinetics, i.e., the potential rate decay for a given pool (in discrete pool models) or SOM of a given quality (in continuum models) is directly proportional to the quantity present (Paustian et al., 1997a). First-order kinetics implies that, all else being equal, the organic matter stabilization efficiency for a given soil is constant and that SOM at steady-state is directly proportional to the rate of organic matter (litter) input. Several lines of evidence now suggest that organic compounds associated with mineral surfaces (clays and oxides), and perhaps organic matter that is physically occluded within aggregates, are subject to saturation in terms of the amount of SOM that can be stabilized (Hassink and Whitmore, 1997; Six et al., 2002; Stewart et al., 2007; Gulde et al., 2008). The phenomenon of saturation represents a fundamental departure from first-order kinetics in that SOM stabilization efficiency is not constant but instead declines with increasing SOM content. Further, with saturation kinetics steady-state SOM content is not directly proportional to organic matter inputs. Instead, SOC saturation results in an asymptotic relationship between whole SOC across increasing C inputs at steady state. It should be clarified that saturation may not be apparent when observed over time but can be observed at steady-state with increasing inputs (Six et al., 2002; Stewart et al., 2007). However, some long-term experiments have shown SOC to respond linearly when the independent variable is C inputs (e.g. Campbell et al., 2001).

Several concepts for representing SOC saturation exist, including direct control from the clay (+ silt) mineral surfaces (Hassink and Whitmore, 1997); the chemical nature and mineralogy of clays (Baldock and Skjemstad, 2000); a whole soil concept including a clay (+ silt) physically protected pool, a microaggregate-protected pool, a

biochemically protected pool, and an unprotected pool (Six et al., 2002); a variable capacity related to a clay (+silt) capacity, C input, aggregate stability, and macro-organic matter (Carter, 2002); and a hierarchical saturation in aggregate sized fractions (Kool et al., 2007; Gulde et al., 2008). However, there are presently very few (if any) formal simulation models that include any of these SOC saturation concepts.

Recently, conceptual models of SOM dynamics have been developed that match model pools with measurable fractions – often identified as addressing the challenge of modeling the measurable or measuring the modelable (Motavalli et al., 1994; Elliott et al., 1996). The pools therein are not defined by kinetics but rather physical, isolatable, or functionally-defined pools and should be isolated by size, density or chemical methods, with distinct differences in biological reactivity (Sohi et al., 2001). Defining pools in this manner has been proposed as a better representation of the actual physical and chemical characteristics of SOM (Christensen, 1996a). Subsequent modeling of SOM dynamics under this convention would be more mechanistic (see Balesdent et al., 2000; Arah and Gaunt, 2001) and reproduce physical protection as described in the current conceptual models of soil aggregation (Buyanovsky et al., 1994; Six et al., 2000).

Building upon the theory and conceptual model of Six et al. (2002) and recent studies by Stewart et al. (2007; 2008b; 2008a), the objective was to develop a simulation model of soil C dynamics, defined by functional (measureable) pools. Until now, the role of soil aggregates in promoting SOM stabilization and potential SOC saturation within SOM models has remained in the conceptual stage, but the proposed model, SATURN (Soil Aggregate **TUR**NOVER or **SATUR**ATION), explicitly includes the formation and turnover of soil aggregates as well as potential SOC saturation.

Methods

Model Structure and Fundamental Concepts

This model is an attempt at ‘modeling the measurable’ (Elliott et al., 1996); and is presented in Figure 2.1. The model does not include a plant-growth submodel, and annual above- and below-ground C additions (plant specific) are specified as a model input (i.e. a driving variable). For annual crops, allometric functions that relate plant biomass partitioning to measured crop yields are used (e.g. IPCC, 2006). However, the inherent decomposability of different plant residues is represented by a plant residue quality index, which defines the quality of residues based on the C:N ratio and the concentrations of both lignin and polyphenols (Tian et al., 1995). These inputs correspond to a structural, resistant residue pool (>2 mm) not included in total SOC calculations (X_1), and a metabolic, more labile SOC pool (X_2). The SOM pools are broadly partitioned into aggregated (>250 μm) and non-aggregated (<250 μm) soil.

Within the non-aggregated soil matrix, SOM exists as fragmented residues; defined as partially decomposed free-particulate organic matter (free-POM), ranging from 53-2000 μm in size. The close association with soil mineral constituents and size distinguish this pool (X_3) from the structural residue (X_1) pool in traditional physical separation methods (Six et al., 1998). Mineral-associated organic matter is derived, in part, from the sorption of microbial biomass, metabolic products and water soluble organic matter (X_2) onto soil minerals (Tisdall and Oades, 1982; Christensen, 2001). The non-aggregated soil mass is comprised of microaggregates (<250 μm) and primary organo-mineral complexes (<53 μm) containing the silt and clay particle size fractions

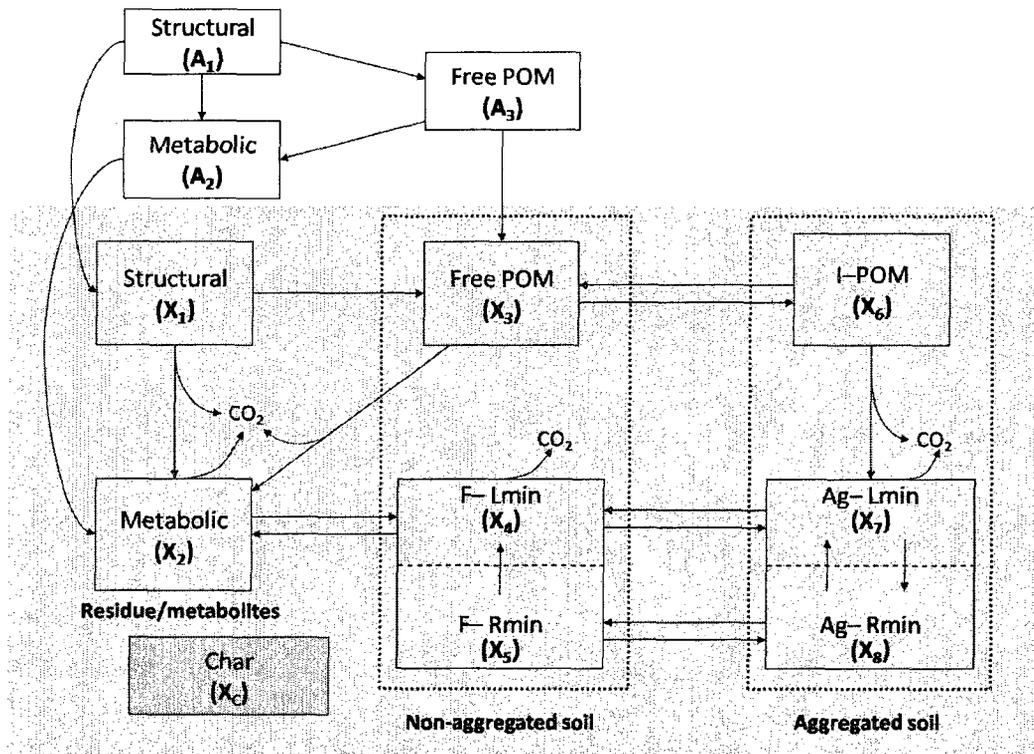


Figure 2.1. Conceptual depiction of the functional pool model. (particulate organic matter =POM; intra-aggregate organic matter =I-POM)

(Elliott, 1986). The organic matter (OM) associated with these mineral constituents is most likely heterogeneous (Elliott and Cambardella, 1991; Buyanovsky et al., 1994); and we have subsequently defined two pools for the mineral-associated OM in non-aggregated soil as labile (X_4) or recalcitrant (X_5).

The aggregated soil (> 250 μm) contains pools analogous to those aforementioned, but these pools are physically protected within macroaggregates and include intra-aggregate particulate organic matter (I-POM) (X_6), and mineral-associated C that is either labile (X_7) or recalcitrant (X_8). The rate of aggregate formation and occlusion of POM is a function of the amount and type of clay minerals minerals (Plante et al., 2006),

as well as the amount of free-POM (Puget et al., 1995; Six et al., 1999). Through aggregate turnover, some I-POM can be released, and with soil disturbances, the rate of I-POM release is significantly increased (Six et al., 1998). Sohi et al. (2005) described both free- POM- (X_3) and I-POM- (X_6) like pools as unique and measurable pools with certain, significant differences in functional C groups revealed from nuclear magnetic resonance spectroscopy. Further, they suggested these two pools should be widely applicable in SOM models.

The final pool, 'char' (X_C), is representative of highly recalcitrant residue, that can have a mean residence time of several thousands of years in soils (Swift, 2001) and has been shown to comprise up to 35% of total organic carbon in some soils (Skjemstad et al., 2002). Despite its relative importance, fractionation and isolation methods for this SOM fraction are still being scrutinized and developed (Skjemstad et al., 1999; Schmidt et al., 2001; Hammes et al., 2007). Currently, this pool is represented as a static quantity in the model, similar to the inert organic matter fraction in the RothC model (Jenkinson et al., 1987). As understanding of the regulatory dynamics between char particles and soil minerals and biota increases from improved methodologies, this pool could be coupled with other processes included in the model such as the sorption desorption process with the metabolic water-soluble fraction (X_2).

The protective capacity provided by silt and clay particles is believed to play an important role in carbon sequestration and is represented in the model as a stabilization process within the aggregated fractions (Hassink, 1996; Six et al., 2002). As I-POM is decomposed, some of the products interact with adjacent mineral surfaces, where they may become chemically protected, in addition to the physical occlusion within newly

formed aggregate structures (Six et al., 1999). Further, disturbances (i.e. tillage) that destroy macroaggregates release I-POM (X_6), microaggregates, and silt and clay particles to the non-aggregated soil matrix. Since we are coupling C dynamics with measurable soil fractions, there is also a direct transfer of C from the aggregated mineral fractions (X_7 and X_8) to the non-aggregated mineral fractions (X_4 and X_5). Following the model of Six et al. (1999), we assume that the only pathway (Fig. 2.1) for C stabilization in the physically protected and highly recalcitrant C pool (X_8) is accomplished through new microaggregate formation within the macroaggregates (Denef et al., 2004). The physically protected pools ($X_{6..8}$) have slower rates of mineralization (see Table 2.1) as a result of physical and chemical protection compared to their analogous non-aggregated pools ($X_{3..5}$) (Besnard et al., 1996; Christensen, 1996b).

The model structure corresponds closely to the conceptual model from Six et al. (2002) which underpins our global hypothesis, where both physical and biochemical protection are important mechanisms in SOM stabilization; and with conservative management and increased residue inputs, SOC saturation may occur. A fractionation scheme to isolate fractions that correspond to pools in the model is presented in Figure 2.2, based upon physical fractionation methods described by Six et al. (1998). Briefly, 8 mm sieved and air-dried soil would be separated by a wet-sieving method described in detail by Elliot (1986); which isolates macroaggregates ($>250 \mu\text{m}$), microaggregates ($>53 \mu\text{m}$), and the silt +clay fraction ($<53 \mu\text{m}$). Aggregate fractions are then suspended in a 1.85 g cm^{-3} sodium polytungstate solution to separate the free-POM fractions from the mineral soil. Next, the 'heavy fraction' is fully dispersed in 0.5% hexametaphosphate solution to separate the I-POM from the mineral fractions (Six et al., 1998).

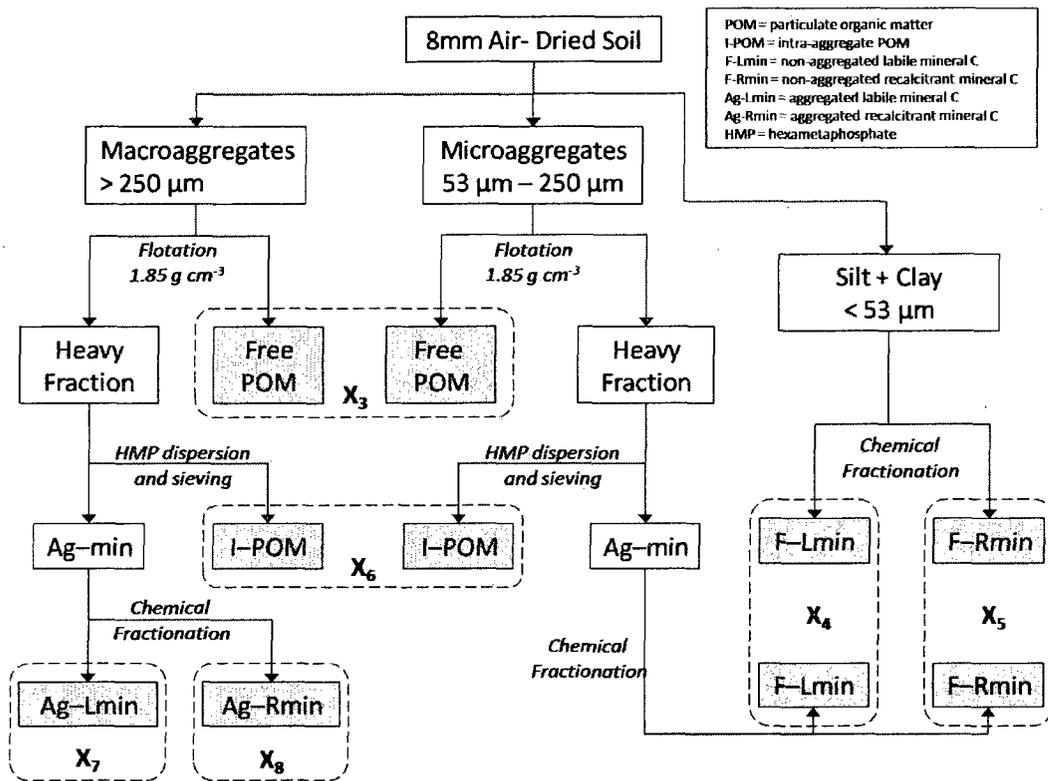


Figure 2.2. Fractionation scheme used to isolate pools for the SATURN model. Shaded fractions are those defined as pools (X_i) within the model.

The final step is to separate the labile and resistant fractions associated with the soil minerals. We have not defined the exact method to be used for the final fractionation, but potential approaches include chemical fractionation (i.e. NaOCl and HF extractions) of the mineral-associated SOM to separate resistant and labile fractions (Leifeld and Kögel-Knabner, 2001; Helfrich et al., 2007; Zimmermann et al., 2007).

Model Derivation

Total SOC (to a default 20 cm depth) is then expressed as the sum of these functionally defined pools:

$$SOC = X_2 + X_3 + X_4 + X_5 + X_6 + X_7 + X_8 + X_C \quad (1)$$

$$TOC_{BG} = SOC + X_1 \quad (2)$$

$$TOC_{AG} = A_1 + A_2 + A_3 \quad (3)$$

which are all expressed in units of g C m^{-2} and where (X_i) are the specified SOC pools belowground; (A_i) are the analogous aboveground pools; (TOC_{AG}) and (TOC_{BG}) are the total organic carbon above- and belowground, respectively (see Fig. 2.1). These pools are linked through processes that include fragmentation, decomposition, aggregate formation/disruption, and sorption/desorption. Residues which are greater than 2 mm (X_1) are typically excluded from SOC stock estimates (Eq. 2) and are often removed during physical fractionation procedures. Aboveground residues (Eq. 3) are subject to first-order decomposition (k_i); with controls from monthly average soil temperature (T) and soil moisture (M). Soil moisture is a function of precipitation and estimated potential evapotranspiration, similar to the conventions used by Parton et al. (1987). We assume that a majority of the transfers described in this model are mediated in part by biological processes, including aggregate turnover. Therefore, the soil temperature and moisture rate modifiers appear throughout the model equations. The equation for each of the aboveground state variables ($A_{1...3}$):

$$\frac{dA_1}{dt} = AGI_S - MT(k_1A_1 - \mu_1A_1 - \Phi A_1) \quad (4)$$

$$\frac{dA_2}{dt} = AGI_M - MT(y_1k_1A_1 - k_2A_2 - \lambda A_1 + y_3k_3A_3) \quad (5)$$

$$\frac{dA_3}{dt} = MT(\Phi A_1 - k_3A_3 - \mu_3A_3) \quad (6)$$

Annual C inputs are representative of the structural (AGI_S) and metabolic (AGI_M) fractions of the residue, determined from an empirical relationship that was derived from the plant residue quality index (see Tian et al., 1995) to partition the residue inputs into the metabolic and structural pools. The aboveground pools ($A_{1...3}$) are analogous to the belowground pools ($X_{1...3}$) and share similar first-order kinetics ($k_{1...3}$), as well as microbial yield coefficients ($y_{1...3}$), with their belowground counterparts (Table 2.1). Larger plant residues (A_I) are subject to fractionation processes (Φ) which yield smaller fragments (less than 2 mm, A_3) and have not yet been quantified in the literature. Just as in the belowground residue fractions described earlier, the water soluble metabolic fraction is termed (A_2). The physical transfer of residues below the surface during tillage, or soil biota activity, are defined (for simplicity) by first-order kinetics (μ_1, μ_3, λ).

$$\frac{dX_1}{dt} = BGI_S + MT(\mu_1A_1 - k_1X_1 - \Phi X_1) \quad (7)$$

$$\frac{dX_2}{dt} = BGI_M + MT(y_1k_1X_1 - k_2X_2 + y_3k_3X_3 + \lambda A_2 + k_D X_4 - k_S X_2 SD_4) \quad (8)$$

$$SD_4 = 1 - \frac{X_4}{(Z_1 \times SL)} \quad (9)$$

Table 2.1. Parameter values and definitions used in the model. (CEC =cation exchange capacity; I-POM = intra-aggregate particulate organic matter; POM =particulate organic matter)

Parameter	Unit	Description
k_1	month ⁻¹	specific rate of decomposition of structural litter
k_2	month ⁻¹	specific rate of C mineralization from free soluble C
k_3	month ⁻¹	specific rate of decomposition of free POM
k_4	month ⁻¹	specific rate of C mineralization from labile, mineral-associated
k_6	month ⁻¹	specific rate of decomposition from intra-aggregate POM
k_7	month ⁻¹	specific rate of C mineralization from labile, aggregate-protected
k_S	month ⁻¹	specific sorption rate of free soluble C
k_D	month ⁻¹	specific desorption rate from labile, mineral-associated C
k_A	month ⁻¹	specific sorption rate into mono-layer recalcitrant fraction
k_Δ	month ⁻¹	specific desorption rate from mono-layer recalcitrant fraction
Φ	month ⁻¹	specific rate of fragmentation of litter
y_1	N/A	yield coefficient of structural C remaining as labile product
y_3	N/A	yield coefficient of free POM C remaining as labile product
y_6	N/A	yield coefficient of I - POM C remaining as labile product
θ	month ⁻¹	specific rate of aggregate formation
γ	month ⁻¹	specific rate of aggregate disruption
sorbmax	g C m ⁻² clay meCEC ⁻¹	maximum rate of sorption of labile, mineral-associated C
cIPOMmax	g I-POM-C g ⁻¹ macroaggregate-associated C	Maximum concentration of I-POM
MLC	g C m ⁻²	'mono-layer' resistant C capacity
----- Site Specific Parameters -----		
Depth	cm	Soil depth
bd	g cm ⁻³	Bulk density
pclay	N/A	Percent clay
SAR	m ² g ⁻¹ clay	Surface area ratio
CEC	cmol _c kg ⁻¹	Cation exchange capacity
Bsat	N/A	Base saturation
Cinput	g C m ⁻² yr ⁻¹	Carbon input

Belowground residues are split into metabolic (BGI_M) and structural (BGI_S) components using the same plant residue quality metrics defined earlier. The continual addition of fresh residues (Eqns. 7 and 8) is essential to new aggregate formation in the conceptual model presented by Six et al. (1999) which served as the conceptual foundation to the model. Here, aboveground residues are transferred belowground and subject to decomposition and sorption (k_S) and desorption (k_D) processes with the mineral

surfaces (e.g. Eqn. 8). The saturation deficit for the free-labile mineral C pool (SD_4 , Eqns. 8 and 9) introduces a feedback control on SOM stabilization dependent upon the proportion of non-aggregated soil (Z_1); to be discussed in greater detail later. Mechanistically, this variable represents potential SOC saturation of the mineral surface (SL) which is a function of soil clay content and clay mineralogy (Hassink and Whitmore, 1997; Six et al., 2002).

$$\varepsilon = \theta \left[1 - e^{(-P_{clay} \times (\alpha \frac{X_3}{SOC} + \beta OX))} \right] \quad (10)$$

$$\frac{dX_3}{dt} = MT[\gamma X_6 - \varepsilon X_3(1 - N) + \mu_3 A_3 + \Phi X_1 - k_3 X_3] \quad (11)$$

$$\frac{dX_6}{dt} = MT[\varepsilon X_3(1 - N) - \gamma X_6 - k_6 X_6 SD_7] \quad (12)$$

Through aggregate formation (ε , Eqn. 10), free-POM (X_3) is incorporated into new aggregates as intra-aggregate POM (X_6). Equations 11 and 12 further show how intra-aggregate POM (I-POM) is returned to the soil matrix by the specific rate of aggregate turnover (γ); which is enhanced by tillage events (Cambardella and Elliott, 1993; Six et al., 1999). Free-POM, by definition, is not physically protected by inclusion within aggregates and is therefore subject to a relatively rapid rate of decomposition (Table 2.1) compared to I-POM (X_6) (Besnard et al., 1996). The maximum rate of new aggregate formation (θ) in Equation 10 is approached by the relationship between the relative proportion of free-POM (Six et al., 1999); the clay content (P_{clay}) and oxide concentration (OX), which contribute to aggregate stability (Kemper and Koch, 1966). In

this equation, terms (α) and (β) are shape parameters. This rate is limited, however, by (N , Eqns. 11 and 12) the ratio of I-POM (X_6) to total macroaggregate-associated carbon ($X_6 + X_7 + X_8$).

$$\frac{dX_4}{dt} = MT(\gamma X_7 SD_4 - \varepsilon X_4 SD_7 + k_5 X_2 SD_4 - k_D X_4 + k_{\Delta} X_5 SD_4 - k_4 X_4) \quad (13)$$

$$\frac{dX_5}{dt} = MT(\gamma X_8 SD_5 - \varepsilon X_5 SD_8 - k_{\Delta} X_5 SD_4) \quad (14)$$

$$\frac{dX_7}{dt} = MT[\varepsilon X_4 SD_7 - \gamma X_7 SD_4 + y_6 k_6 X_6 SD_7 - k_7 X_7 - k_A X_7 SD_8 + k_{\Delta} X_8 SD_7] \quad (15)$$

$$\frac{dX_8}{dt} = MT(\varepsilon X_5 SD_8 - \gamma X_8 SD_5 + k_A X_7 SD_8 - k_{\Delta} X_8 SD_7) \quad (16)$$

The distribution of C across the silt+clay sized C pools is under direct influence from tillage events (i.e. aggregate turnover, γ) and aggregate formation (ε), and also include SOC stabilization controls from our hypothesized saturation constant (SD_i). Equations 15 and 16 include a mechanism of SOM stabilization (i.e. biochemical recalcitrance) afforded within macroaggregates. It is represented by a unique transfer (k_A) between the labile-mineral-associated C and the recalcitrant mineral-associated C pools, (X_7) and (X_8) respectively. The reverse process (k_{Δ} , i.e. destabilization) is present in the analogous pools (X_5) and (X_8), as seen in Equations 13 – 16. An important delineation between the aggregated and non-aggregated pools (Fig. 2.1) is made by dividing the soil into aggregated (Z_2) and non-aggregated (Z_1) states, defined below:

$$\frac{dZ_1}{dt} = MT(-\varepsilon Z_1 + \gamma Z_2) \quad (17)$$

$$\frac{dZ_2}{dt} = MT(\varepsilon Z_1 - \gamma Z_2) \quad (18)$$

These state variables of the model define dynamics for the changes in mass between the aggregated and non-aggregated soil. They are necessary to include because we are coupling C dynamics with physical features of the soil (aggregation) that are dynamic in time. We have proposed a set of simple and linear differential equations (Eqns. 17 and 18) that regulate macroaggregate dynamics, expressed as a concentration (g macroaggregate g⁻¹ soil). We assume the aggregate formation and breakdown processes are controlled, in part, by biological activity. Therefore, we have included soil temperature (*T*) and moisture (*M*) controls (e.g. Eqns. 9, 12-16). Further, the same parameters representing proportional changes in aggregation (ϵ and γ) are applied to the state variables (e.g. Eqns. 9, 12, and 13 – 16) to represent losses or additions of C that are coupled to transfers of soil mass during aggregate formation or breakdown.

$$SD_7 = 1 - \frac{X_7}{(Z_2 \times SL)} \quad (19)$$

$$SD_8 = 1 - \frac{X_8}{(Z_2 \times SR)} \quad (20)$$

$$SD_5 = 1 - \frac{X_5}{(Z_1 \times SR)} \quad (21)$$

In Equations 9 and 19-21, a saturation deficit is defined for the mineral-associated pools (SD_i); which is the difference between the hypothesized saturation level (*SL* or *SR*) and the current size of the appropriate pool. Saturation of the biochemically protected pools (X_5 and X_8) is defined by the specific surface area of the minerals (*SR*); whereas a multi-layered interpretation (*SL*) is used for the arrangement of more accessible organic matter, (X_4 and X_7). Numerous studies have shown that the physically protected C pools (<53 μ m) are subject to saturation when evaluated across increasing C inputs (Kool et

al., 2007; Gulde et al., 2008). According to our definition, the saturation parameters (SL and SR) remain constant over time. These parameters are defined by physical characteristics of the mineral constituents of the entire soil matrix and, by definition, describe a limit to the amount of C that can be stabilized by the whole soil. For this reason, clay content is explicitly expressed in the equations for the saturation parameters. We propose that the (SR) term represents a monolayer assemblage of organic matter to the clay surfaces (Mayer, 1994a, b); and (SL) is defined as a layering of organic matter on the internal monolayer (Kleber et al., 2007). It follows that the magnitude of the saturation parameters is then scaled by (Z_1) or (Z_2), accordingly. Equations 19 and 20 show how the saturation terms are scaled for each pool ($X_{4,5,7,8}$), defining a saturation deficit (SD_i) which is dependent upon the level of aggregation. This derivation ensures that the summation of analogous pools (i.e. X_4 and X_7) does not exceed the saturation limits, in this case (SL).

$$\frac{dX_C}{dt} = -MTk_C X_C \quad (22)$$

Finally, we define the dynamics of the static state variable, the ‘char’ fraction (Eqn. 22). The formation and degradation of the char fraction of soils are not well understood, but it has been suggested to be an important substrate for microbial colonization; which are important in SOM dynamics and can promote the decomposition of more labile organic materials (i.e. X_2) (Hamer et al., 2004). We have applied first-order kinetics (k_C) to this pool (Table 2.1). Even though this pool is not directly coupled with other pools in the model, including it as a static variable lends itself to increased

flexibility for future simulations that may investigate the importance of this pool. Further, an isolation of this fraction can yield direct measurements for the size of this pool, rather than estimating it as a difference between total SOC and the summation of SOM pools.

Results and Discussion

Examination of Saturation and Aggregate Turnover

We have defined saturation mechanisms on the basis of physical characteristics of the soil, namely the surface area ratio of clay minerals available for sorption of organic molecules. The arrangement of OM bound to clay surfaces may exist in layers made of different organic components which may mineralize at different rates, but are physically and chemically protected from microbial attack (Buyanovsky et al., 1994). Alternatively, others have suggested that OM exists in a monolayer arrangement ($0.6 - 1.5 \text{ mg OC m}^{-2}$) on the clay surface, implicating a finite capacity for minerals to complex with OM dependent upon the specific surface area and cation exchange capacity of the clay (Mayer, 1994a; Wiseman and Puttmann, 2005). However, the monolayer hypothesis does not explain the total C content of soils; Chenu and Plante (2006) showed that OM should not be described as a regular coating on individual clay-sized mineral particles and that not all organic molecules of clay-bound OM were in direct contact with mineral surfaces (Kahle et al., 2002; Kaiser and Guggenberger, 2003). Further, Kleber et al. (2007) described the layering of mineral-OM interaction as “zonal structures” of different decomposability and solubility. In the context and scale of this model, the specific, molecular arrangement of the organo-mineral interaction is not directly expressed, but rather the heterogeneous decomposability of this fraction. Clearly the interpretation of the

OM-mineral surface interface could have implications on C dynamics in a mechanistic simulation model. Considering the heterogeneous nature of the mineral-associated C, and apparent C loadings that are in excess of a monolayer equivalent, we have included two pools within this fraction.

In addition to the physical limitations (i.e. mineral surface area) we have defined; saturation can also be examined in terms of increasing C inputs, and observed on a whole soil basis (Stewart et al., 2007) or within individual measurable fractions (Gulde et al., 2008; Stewart et al., 2008a). We ran the model to equilibrium to evaluate steady-state behavior and the underlying characteristics. Initially, we kept all variables constant except C input in order to confirm how total SOC responded to increasing C inputs (Fig. 2.3, Plate A). As expected, all pools reach steady-state given enough time. However, when many simulations are run to steady-state, while iteratively increasing C inputs for each run, the saturation dynamics of the model appear at higher inputs (Fig. 2.3, Plate B). Here, we can observe the linear and non-linear relationships between pools and increased C inputs. Saturation is now observed as the difference between each input rate (at steady-state) is getting smaller as residue input increases. This same relationship has been suggested by others investigating potential SOC saturation (Stewart et al., 2007).

Continuing the method applied in Figure 2.3, Plate B, we ran the model repeatedly, each time with an increasing C input rate. We can collectively evaluate the endpoint (i.e. steady-state) of each run to generate a set of points where C input is the independent variable, not time. These results suggest how the total SOC behaves when simulations are run to equilibrium across many input levels, as in Figure 2.3, Plate C (see also Stewart et al., 2007). The difference between Plate A and Plate C is the dependent

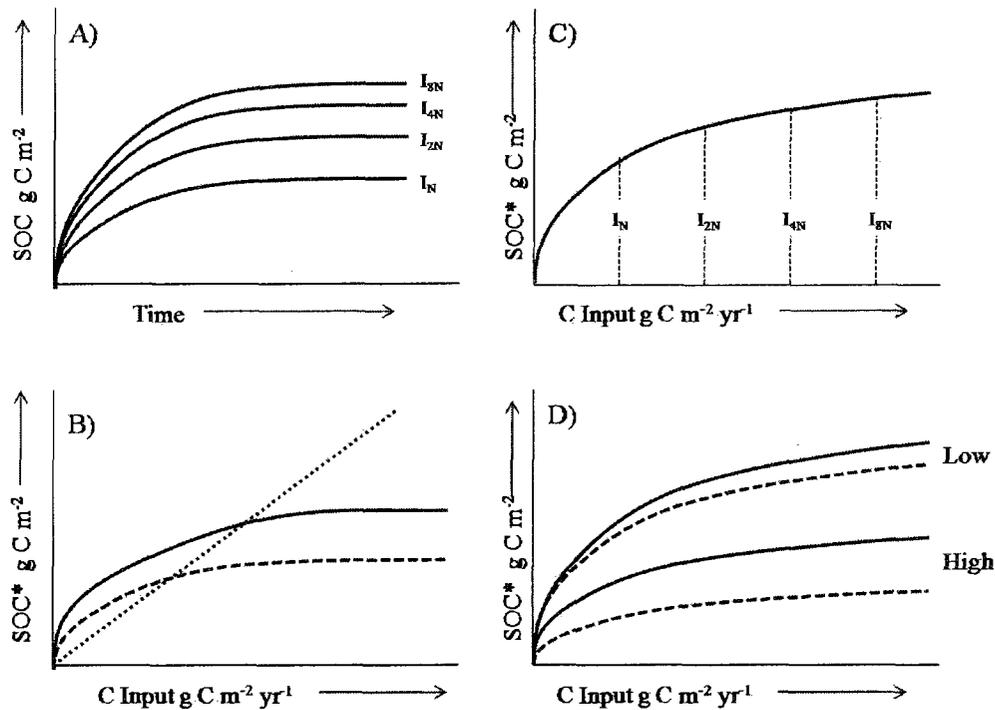


Figure 2.3. Qualitative and descriptive graphs of model behavior. Plate A shows how whole soil organic carbon stocks g C m^{-2} respond to a two-fold increase in annual C inputs (I_N , I_{2N} , I_{4N} , I_{8N}), when the independent variable is time (months). In Plate B soil organic carbon at steady-state (SOC^*) g C m^{-2} is shown for individual fractions that behave linearly (dotted line, e.g. X_3) and others which display saturation (dashed and solid lines, e.g. X_4 or X_8). Plate C depicts whole soil organic carbon stocks g C m^{-2} (again at steady-state) when evaluated over increasing residue inputs $\text{g C m}^{-2} \text{ yr}^{-1}$. Finally, Plate D shows how total SOC at steady-state (SOC^*) is affected by different clay contents (dashed lines = sandy soil, solid lines = high clay soil) in regions with “High” and “Low” average annual decomposition.

variable. For a given climatic region and clay content, the mineral fractions of the soil (those subject to saturation) are important for the long-term stabilization of fresh OM, but as inputs are increased, the linear fractions (i.e. free POM) accumulate the OM; giving the curvilinear shape of the model output. Figure 2.3, Plate D shows how total SOC is affected by different clay contents in regions with contrasting annual decomposition activities. As expected, higher clay contents stabilize more C in the long-term and when

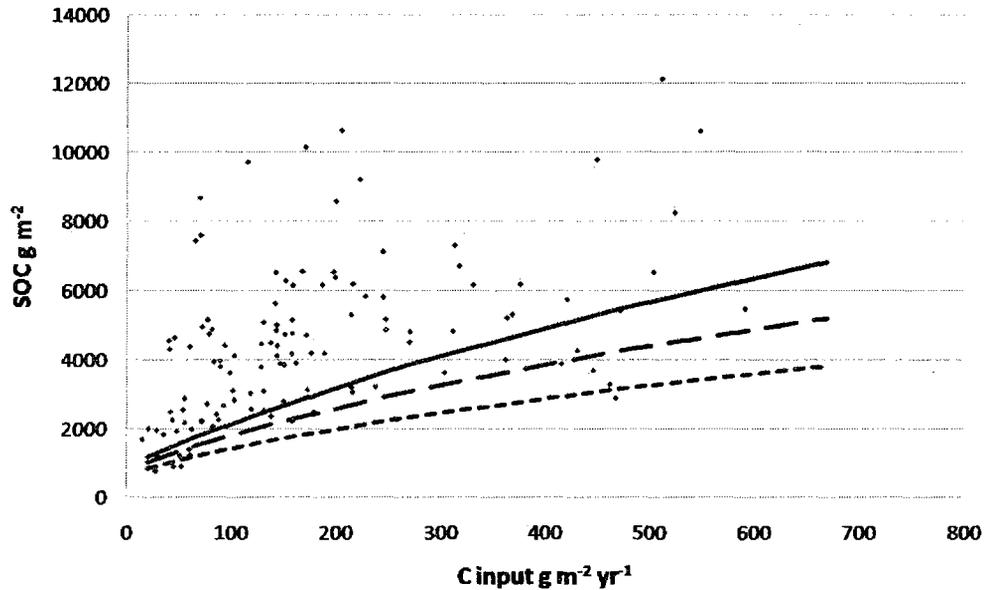


Figure 2.4. Qualitative relationship between C input $\text{g C m}^{-2} \text{ yr}^{-1}$ and soil organic carbon (SOC) stocks g C m^{-2} . Lines represent model generated SOC stocks at steady-state for various C input levels and clay contents (..... = 120 g clay kg soil^{-1} ; - - = 240 g clay kg soil^{-1} ; — = 480 g clay kg soil^{-1}). Measured SOC stocks (\bullet) have been adapted from Stewart et al. (2007).

decomposition is slowed soil C stocks are higher compared to more conducive climates for decomposition. The data points in Figure 2.4, compiled by Stewart et al. (2007) are from a wide variety of locations, including many soil textures and from experiments with different rotations, management treatments and duration. For the simulated data, all conditions remained constant (except C input) and this comparison is purely qualitative and serves to confirm our hypothesis of saturation and that the model produces results that are reasonably close to observed data.

Translating a conceptual model of aggregate dynamics into quantifiable terms required the coupling of C and aggregate (i.e. soil mass) dynamics. We are lacking direct measurements of aggregate formation, but have proposed an empirical relationship based

upon observations central to current conceptual aggregation models. In the proposed rate of aggregate formation (Eqn. 10) we have included the relative availability of free-POM and clay content. In a similar attempt at modeling the measurable, Malamoud et al. (2009) also included clay content and SOC as parameters in their function for aggregation. The presence of fresh particulate organic matter is integral to the process of aggregate formation, and therefore we included (*POM*) as a parameter in the aggregate formation equation. As occluded organic matter is decomposed, the biological activity produces organic substances which are capable of binding soil particles. However, within an aggregate, the same binding effect is reduced through the decomposition of organic binding agents. Therefore, Huang et al. (2005) suggest a continual addition of organic matter is essential to ensure that the contents of aggregating agents are adequate to maintain soil structure stability, which agrees with the aggregate turnover model of Six et al. (2000).

A graphical representation of the relationship between the aggregate formation rate (θ , Equation 10) and clay and oxide contents (g kg^{-1}) is shown in Figure 2.5. Both clay and oxide contents have a positive effect on aggregate formation; however the dependence upon clay content is greater. Our results are corroborated by prevalent understandings of aggregate formation. Carbon enriched clay particles are fundamental to most conceptual soil aggregate models and in relative increases in clay content should result in complexation of clay particles (Edwards and Bremner, 1967; Tisdall and Oades, 1982). In an aggregate formation model proposed by Dexter et al. (2008), there is a positive relationship between clay content and complexed or aggregated carbon. In soils

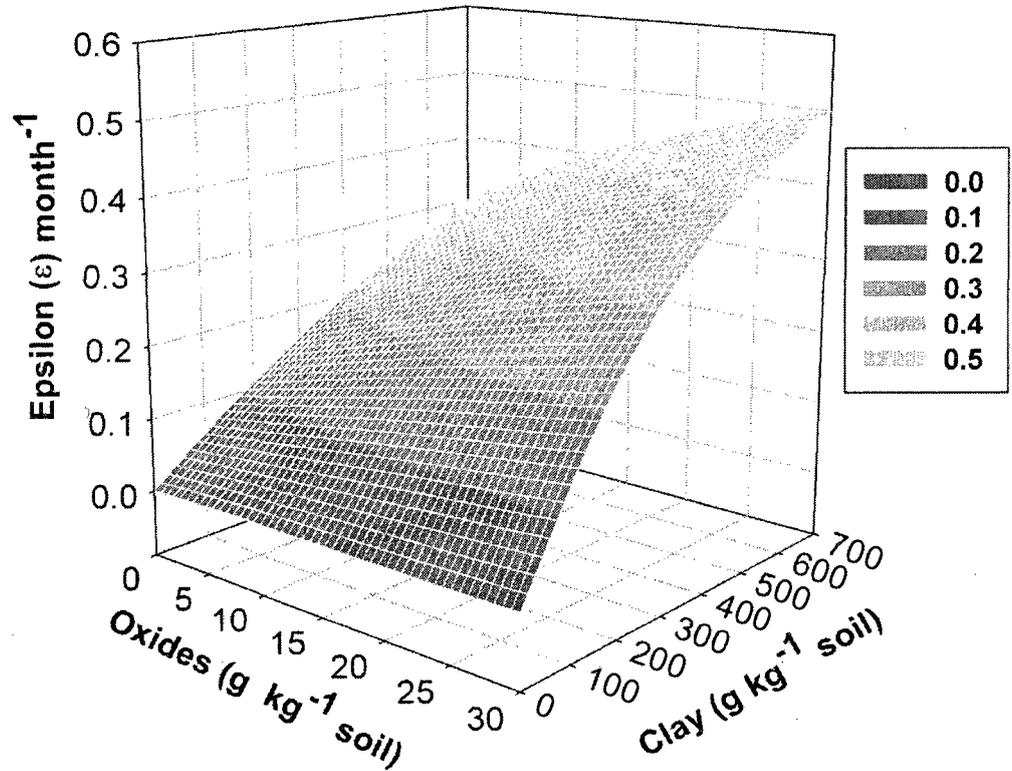


Figure 2.5. Proposed aggregate formation rate function. Clay content (g kg^{-1}) of the soil is shown along the Z-axis, with X-axis displaying the oxide content (g kg^{-1}). Epsilon (ϵ) determines the proportion of non-aggregated soil that becomes aggregated during each time step as shown on the Y-axis. Theta (θ) set equal to 0.6, see Equation 11.

with high SOC contents, clay may be the limiting factor to aggregate formation; conversely in soils with low SOC contents it may be SOC that is limiting.

The spider diagram (Fig. 2.6) is a useful way of demonstrating the sensitivity of an output variable to the controlling parameters and variables (Addiscott, 1993). Here we compare relative changes to the parameter values in the proposed aggregate formation rate shown earlier (Eqn. 10) with subsequent changes in (ϵ), the aggregate formation rate.

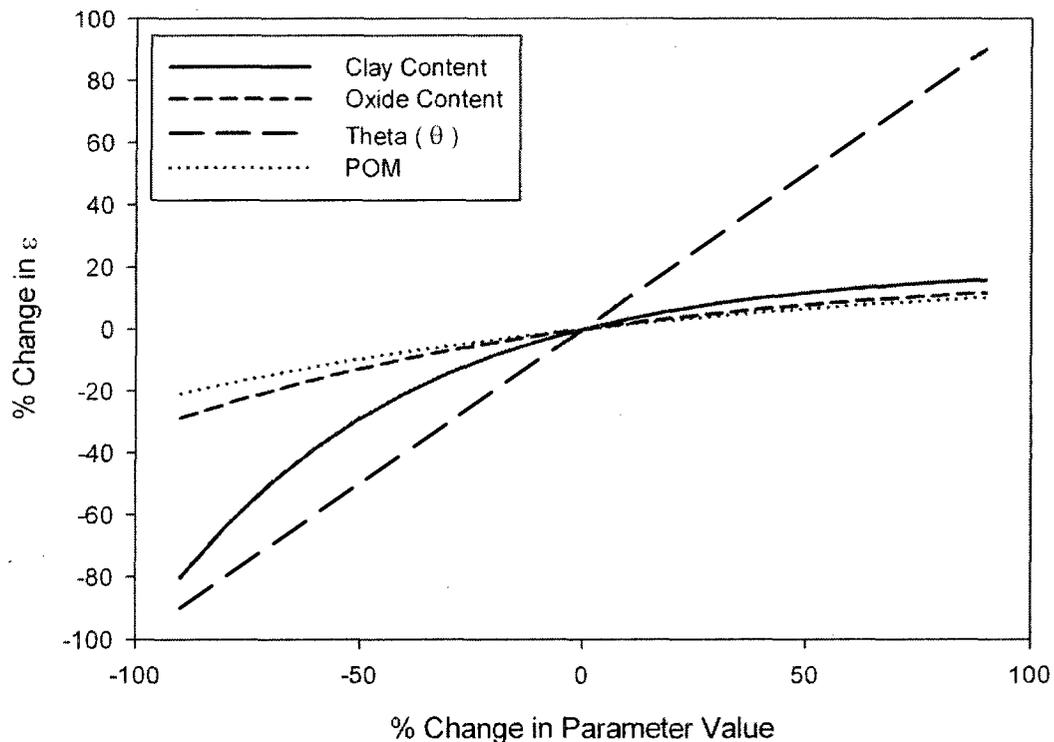


Figure 2.6. Parameter sensitivity of aggregate formation rate (ϵ , Equation 8). Initial values for these parameters were 400 g kg^{-1} soil, 10 g kg^{-1} soil, 0.3 month^{-1} , and 0.04 g for clay content, oxide content, theta (θ), and the particulate organic matter (POM) concentration, respectively. Particulate organic matter concentration is defined as the contributory proportion of POM (X_3) to total soil organic carbon (Eqn. 1).

As expected, there is a linear relationship between theta and epsilon. Epsilon is less sensitive to changes in the other parameters (POM , OX , p_{clay}), especially as their values increase (Fig. 2.6). The initial value for clay content in this figure was 400 g kg^{-1} ; representing a soil with very high clay content. The interesting behavior is at the lower end of the spectrum, when clay contents are low. In this situation, aggregate formation is very sensitive to unit increase in clay content and less sensitive to organic matter (Dexter et al., 2008). Oxide content (OX) is not given much weight from the shape parameter

(beta, Eqn. 10) because in most temperate soils oxide contents (citrate extractable) are negligible. However, in more weathered systems this parameter should be weighted more heavily.

The proposed aggregate formation rate (ϵ), as defined in Equation 10, governs not only the mass transfer between aggregated and non-aggregated soil, but indirectly SOC levels because C is also shifted from physically protected pools to non-aggregated pools during aggregate turnover induced by disturbances (e.g. tillage). Relevant research into an aggregate formation rate has been limited to lab incubations; which aim to quantify new aggregate formation from dispersed soils under ideal conditions over time scales of weeks to months (Gale and Cambardella, 2000; Plante and McGill, 2002a; 2002b; De Gryze et al., 2005). Ideal estimates would be derived from repeated field observations of aggregation levels. These types of observations are not directly measuring aggregate formation but instead taking samples at intervals from which formation rates could be inferred. However the sampling intervals between measurements are probably too coarse to capture aggregate formation occurring at a smaller time scale (e.g. Low, 1955, 1972; Angers, 1992).

Steady-state Analysis of Internal Mechanisms

The complex and nonlinear nature of the model prevented a closed form solution; this limited the ability to directly interpret the relationships between SOC contents and key variables in the model (e.g. clay content, C input, aggregate formation, etc.). However, by running multiple simulations (holding all variables constant except one) to

equilibrium, we were able to qualitatively evaluate how total SOC (or any output pool) responded to any of the variables.

A general and strictly qualitative depiction of how SOC contents are distributed among the pools within the model is shown in Figure 2.7. These relative distributions confirm the effect of tillage management on soil aggregate dynamics. The model was run from native SOC stocks for 100 years to show the effects of conventional tillage (CT) or no-tillage (NT) management. In this scenario the CT treatment consisted of an annual and deep tillage event (assumed tillage to a depth of 20 cm). As seen in Figure 2.7, NT management resulted in less free-POM (X_3), but greater C contents in the aggregated fractions (X_{6-8}). With fewer disturbances in NT management, it is expected that the amount of free POM would be less due to less mixing of surface residues, but total POM ($X_6 + X_3$) would be higher; as suggested by Six et al. (1998) and concurred by the model output (Fig. 2.7). The proportions of the mineral fractions are similar to values (50 – 90% of total SOC) reported in the literature (Jastrow, 1996; Christensen, 2001). Further, there is an increased proportion of non-aggregated mineral C in disturbed soils. The POM (X_3) and soluble metabolic (X_2) fractions of SOC (Fig. 2.7) appear lower than reported values from Cambardella and Elliott (1992). It should be noted that the parameter values of the model were only estimated at this point in the analysis – and this graph only serves as a qualitative assessment of model performance in regards to pool distributions.

Other interpretations of the equilibrium simulations indicated a (near) linear relationship between total SOC and clay content (Figs. 2.8a and 2.8b). Many simulations were run holding parameters constant, varying only clay content on each run. Then, when

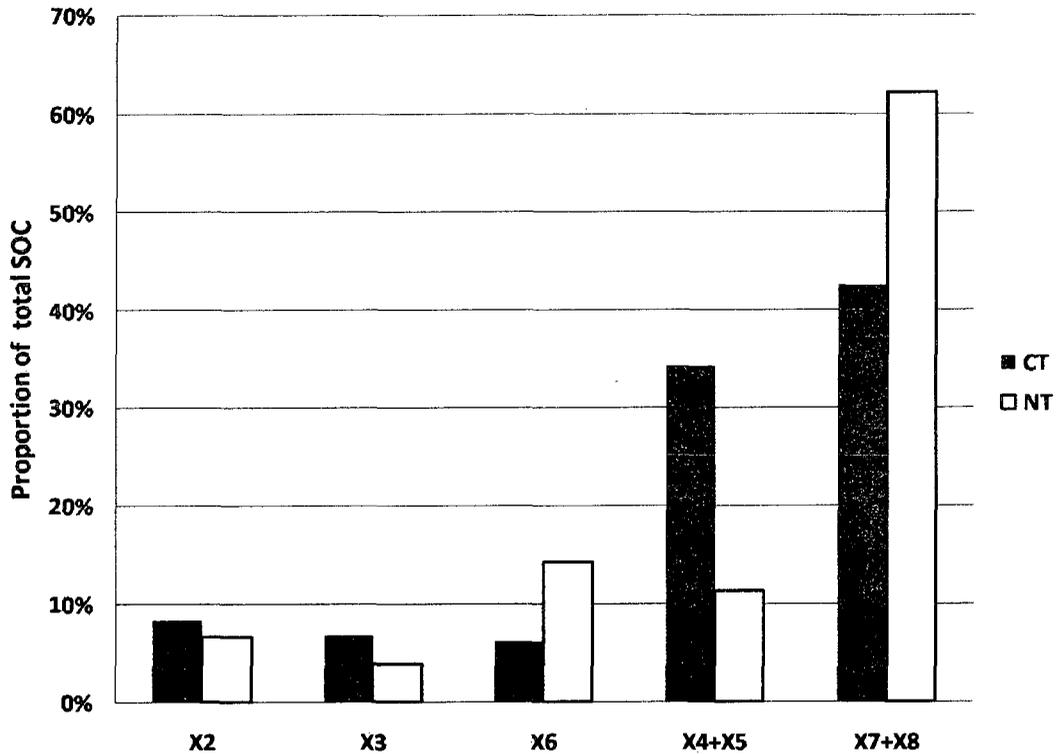


Figure 2.7. Relative proportions of soil organic carbon (SOC) pools. Contributory pools include labile C from metabolic plant residues (X_2); small (<2 mm) particulate organic matter (X_3); the non-aggregated mineral fractions – both labile (X_4) and recalcitrant (X_5); and the aggregated class of SOC pools: intra-aggregate POM (X_6), and labile (X_7) and recalcitrant (X_8) mineral fractions. No-tillage (NT) and conventional tillage (CT) treatments were run for 100 years from native SOC stocks.

evaluating over increasing clay contents, the model output represents the underlying relationship between clay content and total SOC, as determined by the non-linear state equations (Eqns. 9, 12-16). This relationship can be thought of as an ‘unknown function’ which is the net result of the internal dynamics of the model – which cannot be solved numerically. The relationship between total SOC and clay content represents a fundamental component of this model.

We first fit a generic power function and then a best-fit polynomial (Table 2.2) to the model-generated data points, as an attempt to represent the unknown function previously described (Figs. 2.8a and 2.8b). By taking the derivative of the best-fit lines (i.e. the power and polynomial functions) and also a piece-wise derivative between consecutive model points, we gained insight to how SOC contents are changing with respect to a unit change in clay content (Fig. 2.8c). The derivative of the modeled points is very similar to the derivative of the power function ($R^2 = 0.94$, data not shown).

The attenuating derivative (Fig. 2.8c) suggests that the relationship between clay content and whole soil SOC is strongest at lowest clay contents, and decreases as clay contents increase. After evaluating the behavior of the derivative, an interpretation of the original data points generated by SATURN suggests that the relationship is not quite linear, contrary to what others have found (Nichols, 1984; Chenu and Plante, 2006). This conclusion is further supported as the derivative of a linear relationship (function) would be a constant. Similarly, the derivative of the polynomial function (Fig. 2.8c) appeared linear, but the squared term in the polynomial fit was so small in magnitude, that after taking the derivative we were essentially left with a linear function (Table 2.2). Thus, it appears that the derivative of the unknown function does not come from a linear relationship between clay content and SOC.

The derivative of the ‘unknown function’ appears to be unstable in the region of clay contents between 25 – 35 g kg⁻¹; we attribute this to the fact that the function is unknown due to the complex and nonlinear nature of the model – which cannot be solved analytically. Further, we were unable to elucidate the complex interaction of the variables that exist [in the unknown function] which must create this instability. Interpreting SOC

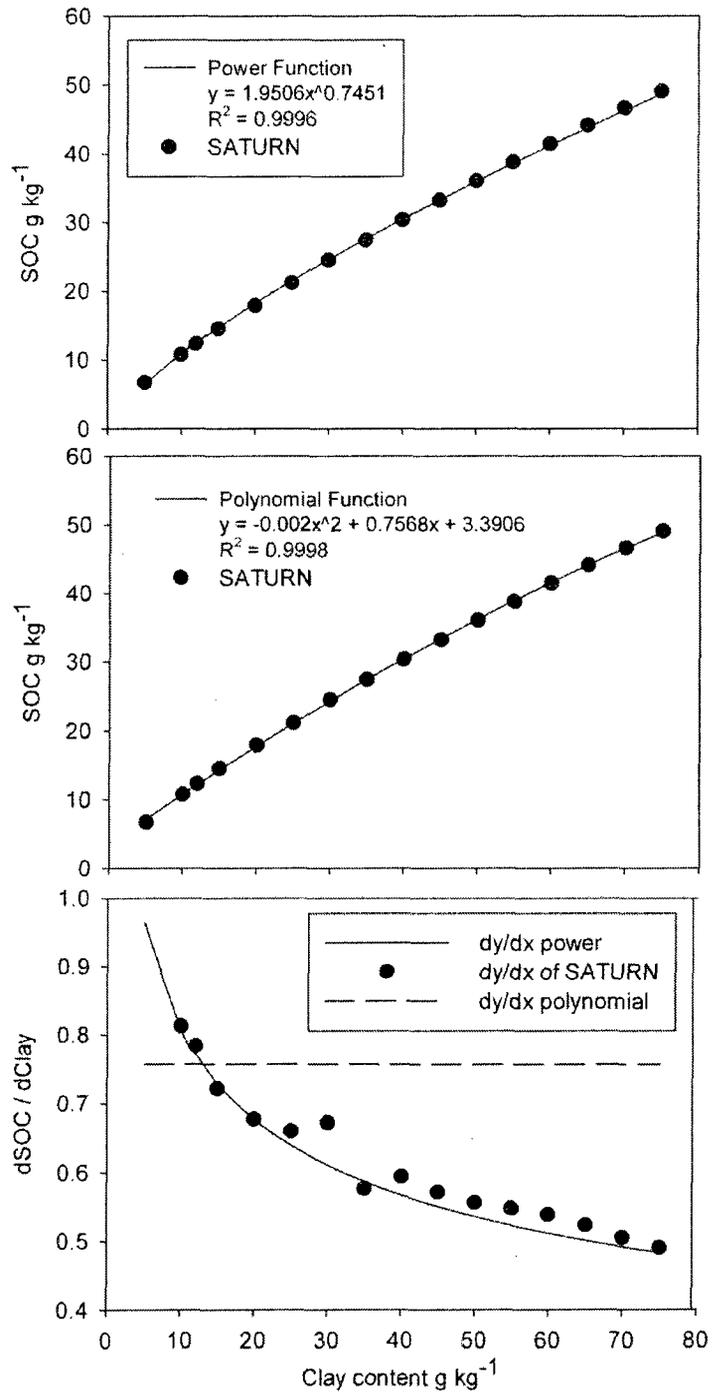


Figure 2.8. Qualitative evaluation of the relationship between clay content (g kg^{-1}) and soil organic carbon (SOC) (g kg^{-1}).

Table 2.2. Equations and derivatives used in the qualitative analysis of the relationship between clay content (x) and soil organic carbon ($f(x)$).

Equation Type	Function	R ²	First Derivative
Linear	$f(x) = 0.5986x + 5.5401$	0.996	$f'(x) = 0.5986$
Polynomial	$f(x) = -0.002x^2 + 0.7568x + 3.3906$	0.9998	$f'(x) = -0.004x + 0.7568$
Power	$f(x) = 1.9506x^{0.7451}$	0.9996	$f'(x) = 1.4534x^{-0.2549}$

contents and potential saturation for a given C input, we conclude that at low clay contents, saturation in the mineral fraction would limit SOC stabilization, and C would then accumulate in the POM fractions. This conclusion is supported by Hassink et al. (1997) and Stewart et al. (2008a) who reported that excess additions of OM (beyond a protective capacity) resulted in an accrual of C in the light and intermediate macro-organic fractions. The apparent increase within the POM fractions keeps the function somewhat linear at higher clay contents (Fig. 2.8c). This further confirms that the relationship between clay and SOC is not linear, similar to inherent properties of other SOM simulation models (RothC and CENTURY, see Paustian et al., 1997b); which do not explicitly include saturation.

Conclusions

The SATURN model presents one of the first examples of a functional pool model. We have defined a set of state variables that are broadly classified into aggregated and non-aggregated pools which allow for direct validation of the state variables with lab measurements. This model is one of the first SOM models to explicitly include the

emerging SOM concepts of saturation and aggregate dynamics. The model also assumes a non-linear relationship between clay content and whole soil C content. We have developed initial approximations for how these concepts can be applied numerically in a simulation model. However, there is not a data set which has been separated according to our proposed fractionation scheme (Fig. 2.2); which prohibits true validation of model performance. Further application of the model to such a data set should elucidate specific parameter values and test our central concepts and assumptions. As it stands now, the relatively inert pool (X_C) is not directly linked to the other pools in the model, and others have taken this approach before (e.g. Jenkinson et al., 1987). When direct measurements of the char fraction are refined and when its dynamics are better understood, it could be linked to other pools in the proposed model.

The implications of whole soil organic carbon saturation on terrestrial C sequestration efforts need to be evaluated when considering mitigation strategies. Often, future scenarios under various management regimes are carried out using simulation models, but current models lack the potential SOC saturation. Research has shown that residue return to the soil does not necessarily increase soil C when the system is approaching steady-state/equilibrium (Hooker et al., 2005); or approaching saturation (Stewart et al., 2007; Gulde et al., 2008).

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C HAPTER THREE

Modeling SOM stabilization processes in agroecosystems: Model parameterization and evaluation

“Art is a lie that makes us realize the truth.”

– Pablo Picasso

Abstract

Current research efforts have led to the development of a new class of models with functional (measureable) pools. In the proposed model, we have explicitly included soil macroaggregate ($> 250 \mu\text{m}$) dynamics; soil organic carbon (SOC) stabilization mechanisms; and the potential for SOC saturation. The model includes nine pools and two other state variables for aggregate dynamics. The objectives are to optimize and evaluate the SATURN model. The model was initially optimized for total SOC content against seven long-term (>12 years) agroecosystem experiments; containing contrasts in tillage management (a mechanism for aggregate turnover) and different in crop rotations with a SOC gradient across sites of approximately $5 - 25 \text{ g C kg}^{-1}$ soil. The final optimized values resulted in a root mean square error for total SOC of 1.2 g C kg^{-1} soil across all seven sites. The model differentiated no-till and conventional tillage treatments at the Hoytville, OH site, where measured differences were the greatest. However, the model is not predicting temporal SOC changes under NT within sites. This analysis is limited to the total SOC content and individual pool sizes were not optimized against measured data, which limits the degree to which we can truly validate the internal dynamics of the model; an added benefit of measureable pool models.

Introduction

Research during the past decade has fostered new conceptual models of soil aggregate dynamics (e.g. Six et al., 1999) and mechanisms of soil organic matter (SOM) stabilization in mineral soils (Jastrow et al., 2007). These conceptual models can provide foundation for simulation models which can then articulate, in greater detail than previously, mechanisms involved in stabilization and consequences for whole SOM dynamics. SATURN is a new mathematical model that incorporates three concepts relating to SOM stabilization that have generally not been included in widely used simulation models of SOM dynamics: 1) soil aggregate dynamics and aggregate-protection of OM; 2) surface area and mineralogy of clays and oxides as controls on SOM stabilization on mineral surfaces; and 3) saturation kinetics of surface- and aggregate-associated SOM.

Soil aggregate turnover (both macro- and micro-) can explain the mechanisms (physical protection and biochemical recalcitrance, respectively) of SOM stabilization. Briefly, macroaggregates provide physical protection of particulate organic matter (POM) and promote the formation of microaggregates (within the macroaggregates). Microaggregates are more stable (i.e. longer turnover times) than macroaggregates and therefore provide prolonged protection of SOM (Six et al., 2000b). The aggregate distribution of the soil, a dynamic feature, has been shown to capture management effects (tillage vs. non-tillage) (Beare et al., 1994a); over both long and short time spans (Wright and Hons, 2005; Olchin et al., 2008); and in soils with different mineralogy (Denef et al., 2004).

Further, soil aggregates and other SOC fractions obtained from conventional physical and chemical fractionation schemes should reveal measurable properties of the soil that are indicative of past management (those fractions with longer residence times) and the current 'state of the system' (those fractions with shorter residence times). This speculation has been corroborated by aggregate turnover research utilizing stable isotopes (Christensen and Sørensen, 1985; Puget et al., 1995). Briefly, this research confirmed the role of fresh organic matter (OM) in the formation of new macroaggregates, and slower turnover time of microaggregates. Thus, fresh OM is an integral part of new aggregate formation and the distribution of carbon between fractions (with different turnover rates) can be indicative of management.

Another mechanism for SOM stabilization is afforded by the close association of SOM with the mineral (clay and silt) components of the soil; which is different from the innate degradability of SOM. The mechanisms for the slower (default) decay constants are usually implied (e.g. 'physically protected') or related to texture in conventional, kinetically-defined models (Jenkinson and Rayner, 1977; van Veen and Paul, 1981; Parton et al., 1987; Verberne et al., 1990).

As described above, the concept of organo-mineral interaction has been included in simulation models before, but in a limited manner where it served to effectively slow down decomposition processes. However, recent research suggests that these organo-mineral complexes may become saturated in terms of the amount of SOM that can be stabilized (Stewart et al., 2007). This concept has important implications for soil C sequestration as a greenhouse gas mitigation option because of direct limits to the amount of C that could be sequestered. Assuming saturation exists, equilibrium does not

necessarily mean the protective capacity (saturation) of the soil has been reached, but rather C inputs and decomposition processes have reached steady-state. By our definition, saturation would be evident if increased residue input resulted in an accumulation of particulate organic matter, not stabilized (mineral-associated) C; similar to the concepts proposed by Hassink et al. (1997) and reviewed by Six et al. (2002).

In addition to explicit inclusion of stabilization mechanisms, the proposed model is comprised of measureable or isolatable SOM pools. The idea of making models comprised of measureable pools, rather than kinetically-defined, was termed 'modeling the measureable' by Elliott et al. (1996); and according to Hassink (1995) would allow for a better representation of SOM in simulation models. Paustian (1994) further explains, noting that the major constraint for existing process-orientated models is a lack of functional characterization of SOM pools which closely correspond to experimentally determined fractions. In addition to new model development (e.g. Sohi, 2001; Malamoud et al., 2009), there have been efforts to re-align, or retrofit current models with measureable pools (see Skjemstad et al., 2004; Zimmermann et al., 2007); indicating the importance and added benefits of the enhanced validation and verification.

Providing a fractionated soil sample (which aligns with model pools) could serve as direct measurements of the state variables. This differs from some current SOM models, the results of which are often compared to whole soil total organic carbon measurements because the internal pools are not directly measurable (Elliott et al., 1996). The process of linking fractions from chemical or physical separations with kinetically-defined pools may prove to be a significant challenge and has had mixed results in the past, as noted by Parton et al. (1996). They go on to explain that some of the chemically

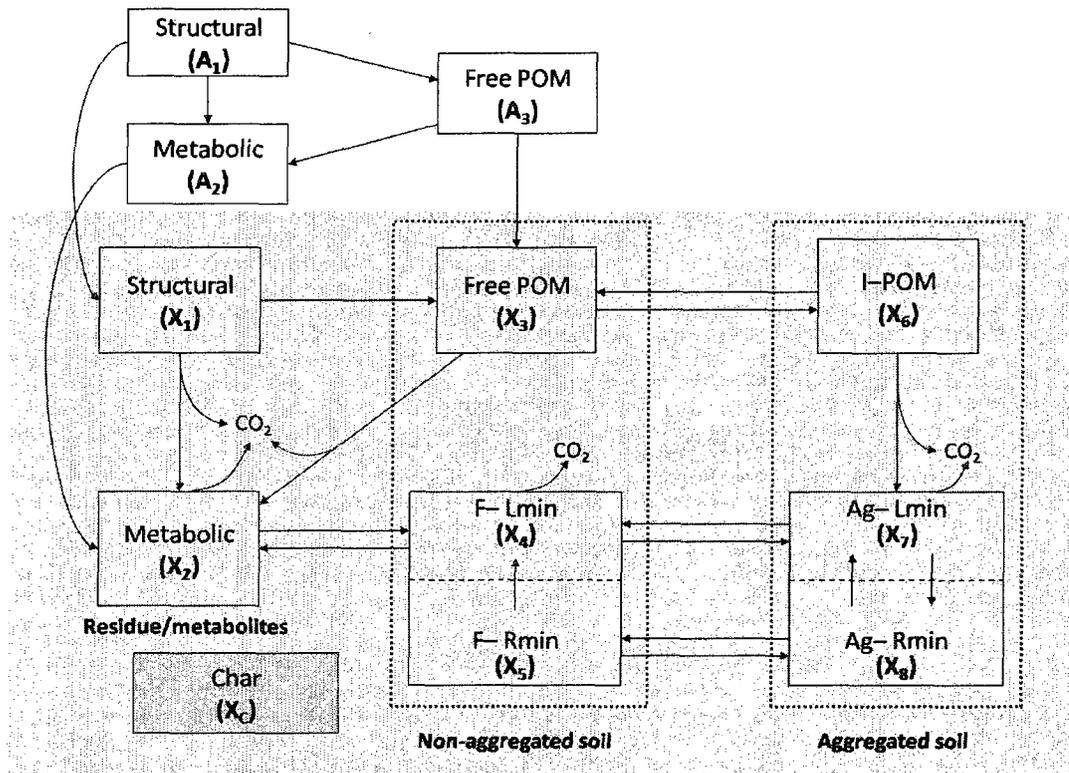


Figure 3.1. Conceptual depiction of the functional pool model, SATURN. Shaded area denotes belowground pools (X_i , X_C), and the associated aboveground pools (A_i). Free particulate organic matter (Free POM; X_3) is distinguished from intra-aggregate organic matter (I-POM; X_6) by the dotted lines. Similarly, two distinctions are made within the mineral associated C: 1) non-aggregated mineral C is split into labile (F-Lmin, X_4) and recalcitrant (F-Rmin, X_5) fractions; 2) aggregated mineral C is likewise split into labile (Ag-Lmin, X_7) and recalcitrant (Ag-Rmin, X_8).

isolated fractions do not always display first-order kinetics, a common assumption of SOM simulation models.

The objectives of this chapter are to optimize and evaluate the SATURN model (Fig. 3.1), developed in detail by Olchin et al. (2009). The model will be optimized against a suite of data from long-term agroecosystem experiments in North America across a climatic gradient to improve model generality. The sites were selected to have consistent management regimes and varying soil textures (a key variable in the model);

described in detail by Paul et al. (1997). The SATURN model presents a fundamental step towards a complete functional pool model. This is an initial optimization and evaluation of the model performance against whole soil C dynamics. Thus, a more detailed evaluation on individual pools using measurements from appropriate fractionation studies is a logical next step.

Materials and Methods

Model Description

The SATURN model has been previously described in detail (see Olchin et al., 2009); thus only a brief description is given here (Fig. 3.1). Fresh residues added to the soil are split between resistant structural (X_1) and labile metabolic components (X_2); as a function of residue quality. As coarse residues (X_1 ; >2 mm) fragment they are transferred into the particulate organic matter (POM) pool (X_3 ; <2 mm). The occluded POM fraction (X_3) can become incorporated within macroaggregates as intra-aggregate POM (X_6), where it is subject to slower decomposition rates and has the potential to promote new microaggregate formation (Oades, 1984; Besnard et al., 1996; Six et al., 2000a). The mineral associated SOC pools are subdivided into a labile (X_4 or X_7) and resistant (X_5 or X_8) fraction, as suggested by Balesdent et al. (1988) and discussed in the previous chapter. More importantly, the labile and resistant groups of mineral-associated SOC are limited by different saturation parameters, (SL) and (SR), respectively (Olchin et al., 2009). A more significant split is made to differentiate the C associated with aggregated (X_7 and X_8) and non-aggregated soil (X_4 and X_5). Thus, and for example, (X_4) is non-

aggregated labile mineral associated C and (X_8) is aggregated recalcitrant mineral associated C.

We do not explicitly model microaggregate dynamics, but have designated mineral associated C pools (X_7 and X_8) located within the aggregated proportion of soil. According to Six et al. (2002), microaggregates provide the mechanism for biophysical protection, and this is represented in the schematic (Fig. 3.1) by the transfer (arrow) from the labile mineral associated C (X_7 , Ag-Lmin) to the recalcitrant mineral associated pool (X_8 , Ag-Rmin). Following the aggregate turnover model of (Six et al., 1999), new microaggregates are only formed within macroaggregates. Accordingly, this process is not present between the non-aggregated pools (X_4 and X_5). However, there is no direct decomposition of the recalcitrant mineral-associated C pools (X_5 and X_8) as a means of including the biophysical mechanisms without another pool for microaggregates.

$$X_4 + X_7 < S_L \quad (1)$$

$$X_5 + X_8 < S_R \quad (2)$$

By modeling the aggregation as a proportion of soil, we can couple aggregation and SOC dynamics – which would be an implied trait of a model with pools derived from physical fractionation of whole soil. Therefore, changes in aggregation result in differences between the physical location (i.e. aggregation state) of SOC as well as the decomposability. Under this tenet, at any given time, the sums of corresponding pools never exceed the saturation parameters (S_L) and (S_R) (Eqns. 1 and 2). The saturation parameters represent the two major hypotheses for the interaction between organic matter



Figure 3.2. Locations of the long-term agroecosystem sites used for the optimization procedure.

and mineral surfaces; a monolayer assemblage (Mayer, 1994a, b); and an outer layering of organic matter on the internal monolayer (Kleber et al., 2007). These hypotheses present mechanistic interpretations of the saturation concepts proposed by others (e.g. Hassink, 1996).

Site Descriptions

For the optimization and initial calibration of the model, we selected seven long-term sites with contrasting tillage treatments (conventional vs. no-tillage management) and common crop rotations (e.g. continuous corn or wheat-fallow); which also represented a climatic gradient (Fig. 3.2). The combined effects of monthly average soil moisture and temperature controls on the biologically mediated processes in the model are shown in Figure 3.3, showing the annual climatic differences among these seven sites.

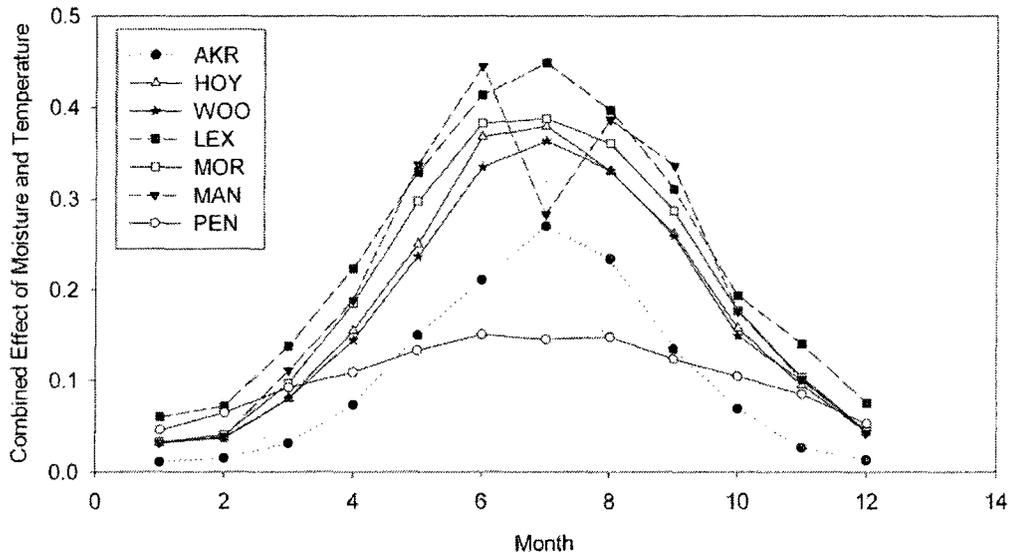


Figure 3.3. Combined effects of moisture and temperature controls at the long-term agroecosystem sites used in the optimization procedure: Akron, CO (AKR); Hoytville, OH (HOY); Wooster, OH (WOO); Lexington, KY (LEX); Urbana, IL (MOR); Manhattan, KS (MAN); Pendleton, OR (PEN).

The soil moisture and temperature functions were described in Olchin et al. (2009). These sites vary in clay content from 120 – 370 g kg⁻¹ and the data we used had been under the respective treatments for a range of 13 – 118 years (Table 3.1). Including such a broad range of climatic controls, clay contents, and management histories should help to support the generality of the model.

Contrasting tillage treatments within Lexington, KY; Wooster, OH; and Hoytville, OH were under continuous corn management since 1975, 1962, and 1962, respectively. Across all sites, no-tillage (NT) consisted of no soil disturbance other than planting. The conventional tillage (CT) treatment at both Lexington and Wooster consisted of a spring tillage event 20-25 cm deep, the later having an additional 10 cm in the month prior to planting; Hoytville had an additional deep tillage event each fall

(Blevins et al., 1977; Dick et al., 1986b; Dick et al., 1986a). The Morrow Plots located near Urbana, IL have been under continuous corn since 1876 with the same tillage treatment as described for Lexington. Data from the original unfertilized plots (3NA and 3NC) were used in this analysis (Odell et al., 1984). Long-term data from the continuous soybean rotations initiated in 1974 at Manhattan, KS were included to represent crop residues of slightly higher quality. At this site CT was a fall tillage (chisel plow) and a spring disking (Havlin et al., 1990). Rotations from Akron, CO and Pendleton, OR had been under wheat-fallow management since 1982 and 1931, respectively (Collins et al., 1992; Halvorson et al., 1997). At the Pendleton experiment, CT was defined as spring moldboard plow up to 20 cm deep, followed by four additional rod-weeder passes (5-7 cm deep) during the summer fallow (Rasmussen and Parton, 1994). Finally, the CT treatment at Akron was stubble-mulch tillage with an average of six sweep and rod-weeder operations during the fallow period. A majority of the data were catalogued in Paul et al. (1997); Table 3.1 contains additional and original references of these long-term experiments, when available.

Model Calibration and Optimization

The model was optimized against an independent data set for parameter fitting. We used the Premium Solver Platform v8.0 (Frontline Systems Inc., Incline Village, NV, USA) add-in for the optimization routine which sought to minimize the root mean square error (*RMSE*, Eqn. 3) between measured and modeled data; where N is the number of observations, P and O are measured and observed values, respectively. This software allowed for simultaneously optimization against data from each of the long-term

Table 3.1. Relevant characteristics of the sites (from east to west) used during the optimization process. Supplementary data and full summaries of each of these long-term agroecosystem experiments available from Paul et al. (1997).

Site [†]	Tillage Regimes [†]	Duration [§] -- yrs --	Treatment [§]	Crop	Number of Samples	Clay Content --- g kg ⁻¹ ---	Geographic Location	Additional References
Wooster, OH (WOO)	CT and NT	34	None	Cont. Corn	8	150	40° 48' N 82° 0' W	Lal et al. (1994) Six et al. (1998) Haile-Mariam et al. (2008)
Hoytville, OH (HOY)	CT and NT	33	None	Cont. Corn	4	370	41° 00' N 84° 0' W	Haile-Mariam et al. (2008)
Lexington, KY (LEX)	CT and NT	33	0 kg N ha ⁻¹ 84 kg N ha ⁻¹	Cont. Corn	16	120	38° 07' N 84° 29' W	Blevins et al. (1983) Elliott et al. (1994) Ismail et al. (1994) Six et al. (1998) Deneff et al. (2004)
Urbana, IL (MOR)	CT only	118	None	Cont. Corn	10	250	40° 6' N 88° 13' W	Dannody and Peck (1997) Aref and Wander (1998)
Manhattan, KS (MAN)	CT and NT	13	None	Cont. Soybean	2	264	39° 7' N 96° 37' W	Havlin and Kissel (1997)
Akron, CO (AKR)	CT and NT	26	None	Fallow – Wheat	6	310	40° 19' N 103° 9' W	Halvorson et al. (1997)
Pendleton, OR (PEN)	CT only	65	Stover + N	Wheat – Fallow	24	240	45° 44' N 118° 37' W	Rasmussen and Parton (1994) Rasmussen and Smiley (1997) Rasmussen et al. (1998)

† Three-letter abbreviations for each site appear in parentheses

‡ Conventional Tillage (CT); No-tillage (NT)

§ Duration of experiment over which we selected measurements and ran the simulation

|| Number of samples refers to the total number of measurements across treatments within each site that were used in the optimization procedure

||| The additional references were used to gather relevant site characteristics and C data from various sampling times

Table 3.2. Parameter values and definitions used in the model. Optimized values are **bold** and underlined.

Parameter	Value	Unit	Description	Documented Range	Supporting Documentation
k_1	<u>0.047</u>	month ⁻¹	specific rate of decomposition of structural litter	0.083 – 0.833	Parton et al. (1987)
k_2	<u>0.161</u>	month ⁻¹	specific rate of C mineralization from free soluble C	0.016 – 0.083	Parton et al. (1987)
k_3	<u>0.056</u>	month ⁻¹	specific rate of decomposition of free POM	0.035 – 0.09	(Buyanovsky et al., 1994; Balesdent et al., 1998)
k_4	<u>0.0034</u>	month ⁻¹	specific rate of C mineralization from labile, mineral-associated	0.45	Hassink and Whitmore (1997)
k_6	<u>0.0093</u>	month ⁻¹	specific rate of decomposition from intra-aggregate POM	0.035 – 0.09 0.011	Hassink and Whitmore (1997) Hassink and Whitmore (1997)
k_7	<u>0.0005</u>	month ⁻¹	specific rate of C mineralization from labile, aggregate-protected	0.001 – 0.0017	Buyanovsky et al. (1994)
k_C	0.000001	month ⁻¹	specific rate of C mineralization from the 'char' fraction	0.0016 – 0.016	John et al. (2005) Carter (1995)
k_S	<u>0.0079</u>	month ⁻¹	specific sorption rate of free soluble C	0.00008 – 0.0002	Buyanovsky et al. (1994)
k_D	<u>0.0011</u>	month ⁻¹	specific desorption rate from labile, mineral-associated C	0.00008 – 0.0002	(Skjenstad et al., 1996; Hammes et al., 2008)
k_A	<u>0.006</u>	month ⁻¹	specific sorption rate into mono-layer recalcitrant fraction	0.00008 – 0.0002	Buyanovsky et al. (1994)
k_{Δ}	<u>0.0015</u>	month ⁻¹	specific desorption rate from mono-layer recalcitrant fraction	0.00008 – 0.0003	(Skjenstad et al., 1996; Hammes et al., 2008)
Φ	<u>0.01</u>	month ⁻¹	specific rate of fragmentation of litter	N/A	Hassink and Whitmore (1997)
Y_1	0.4	N/A	yield coefficient of structural C remaining as labile product	0.0925	Hassink and Whitmore (1997)
Y_3	0.4	N/A	yield coefficient of free POM C remaining as labile product	0.0012	Hassink and Whitmore (1997)
Y_6	0.4	N/A	yield coefficient of I - POM C remaining as labile product	N/A	Hassink and Whitmore (1997)
m_1	<u>0.2099</u>	month ⁻¹	translocation rate of structural C from aboveground to belowground	N/A	
λ	<u>0.0747</u>	month ⁻¹	translocation rate of metabolic C from aboveground to belowground	N/A	
m_3	<u>0.0882</u>	month ⁻¹	translocation rate of POM C from aboveground to belowground	N/A	
θ	0.21	month ⁻¹	specific rate of aggregate formation	N/A	
γ	0.04	month ⁻¹	specific rate of aggregate turnover	N/A	
sorbmax	0.0002	**	maximum rate of sorption of labile, mineral-associated C ** g/m ² clay surface/me.CEC	N/A	
cIPOMmax	<u>0.6588</u>	N/A	Maximum concentration of I-POM (g C POM / g C macros)	0.04 – 0.06	Jastrow (1996)
MLC	0.00085	g C m ⁻²	'mono-layer' resistant C capacity	0.0005 – 0.0015	(Mayer, 1994; Christensen, 2001)
α	<u>4.366</u>	N/A	shape parameter within the aggregate formation rate equation		
β	<u>0.2099</u>	N/A	shape parameter within the aggregate formation rate equation		

agroecosystem experiments (Table 3.1). Initial constraints were set at $\pm 50\%$ of the hypothesized parameter values, but these bounds were exceeded in some cases. Table 3.2 identifies the parameters of interest for the optimization procedure: the first-order decomposition constants ($k_{1,2,3,4,6,7}$); the fragmentation rate of structural litter (ϕ , Φ) as no values from the literature could be found; the translocation constants from above- to belowground pools (m_1 , λ , m_3); the maximum concentration ($c_{IPOMmax}$) of I-POM C (X_6) relative to macroaggregate C ($X_6+X_7+X_8$); and the two shape parameters from the aggregate formation rate (α and β).

$$RMSE = \sqrt{\frac{\sum_{i=1}^N (P_i - O_i)^2}{N}} \quad (3)$$

In many conventional models (Jenkinson et al., 1987; Parton et al., 1987) the SOM pools have mean residence times of centuries to millennia. One approach to initialize these pools is to run the model to (near) equilibrium, i.e. for several thousand years to initialize. However, if the sizes of the pools within a model can be directly measured from a fractionated soil, there would be no need to ‘spin-up’ or equilibrate the model before simulations start. Our data, taken over the span of each experiment (Table 3.1) did not include measured fractions corresponding to specific model pools (Fig. 3.1). Therefore, we ran the model to equilibrium at each site with approximate C inputs to reach a SOC concentration that was close to the initial measurements at each site; thus excluding the initial measurements at each site (when available) from the optimization procedure. Accurate C inputs prior to the onset of these experiments are difficult to

estimate if there was no prior cultivation, because direct measurements do not exist. For the spin-up, we used C input values within a range of historic C input values from Century and prior yield data from before the onset of these long-term experiments (Steve Williams, personal communication 2009).

Results and Discussion

Previously, Olchin et al. (2009) defined non-aggregated (Z_1) and aggregated (Z_2) states/proportions of the soil (Eqns. 4 and 5). These state variables are governed by aggregate formation and breakdown, epsilon (ϵ) and gamma (γ), respectively; with influence from soil moisture (M) and temperature (T) controls (Olchin et al., 2009). The steady-state solution to Equations 4 and 5 is shown in Equation 6, which shows that the specific rates of aggregate formation and turnover are directly proportional to the aggregation states (Z_1 and Z_2) at steady-state.

$$\frac{dZ_1}{dt} = MT(-\epsilon Z_1 + \gamma Z_2) \quad (4)$$

$$\frac{dZ_2}{dt} = MT(\epsilon Z_1 - \gamma Z_2) \quad (5)$$

$$\frac{\epsilon}{\gamma} = \frac{Z_2}{Z_1} \quad (6)$$

$$\epsilon = \theta \left[1 - e^{(-P_{clay} \times (\alpha \frac{X_3}{SOC} + \beta OX))} \right] \quad (7)$$

The rate of aggregate formation (ϵ , defined Eqn. 7) is enhanced by clay (P_{clay}) and oxide contents (OX), in addition to the relative proportion of POM (X_3) to whole soil organic carbon (SOC); but does not exceed a proposed specific rate of aggregate formation (θ). The other parameters, alpha (α) and beta (β) are shape/scaling parameters for the function.

Under our assumptions, a maximum aggregation level exists; supported by research showing that over a range of clay content, and neglecting oxide-rich soils, macroaggregates reach a maximum concentration of soil mass around 85 – 95% (Jastrow, 1996; Six et al., 2000b). Given the equilibrium condition (a maximum aggregation level where $Z_2 = 0.85$); epsilon must always be 5.66 times greater than gamma (Eqn. 4). As long as the proportion between epsilon and gamma remains constant, the length of time it takes the system to recover from a disturbance can be adjusted by changing the magnitude of epsilon (or gamma). At any given point in time, the aggregation state of a soil is the net result of aggregate formation and breakdown, with both processes occurring independently. In this mathematical interpretation of aggregate turnover, both processes are represented, allowing for the flexibility to increase the breakdown rate of aggregates during tillage events (or other disturbances), without affecting the nominal aggregate formation rate. However, we can evaluate the relationship between the aggregate formation rate and the resilience of the aggregates (Fig. 3.4). Here we have defined ‘resilience’ as the time it takes (Z_1) and (Z_2) to return to equilibrium ratios after a tillage event, all things remaining equal. Assuming values of 0.21 and 0.04 for epsilon and gamma, and following a single and intense tillage event, the system approaches the previous state of aggregation in approximately 20 – 25 months (optimal conditions).

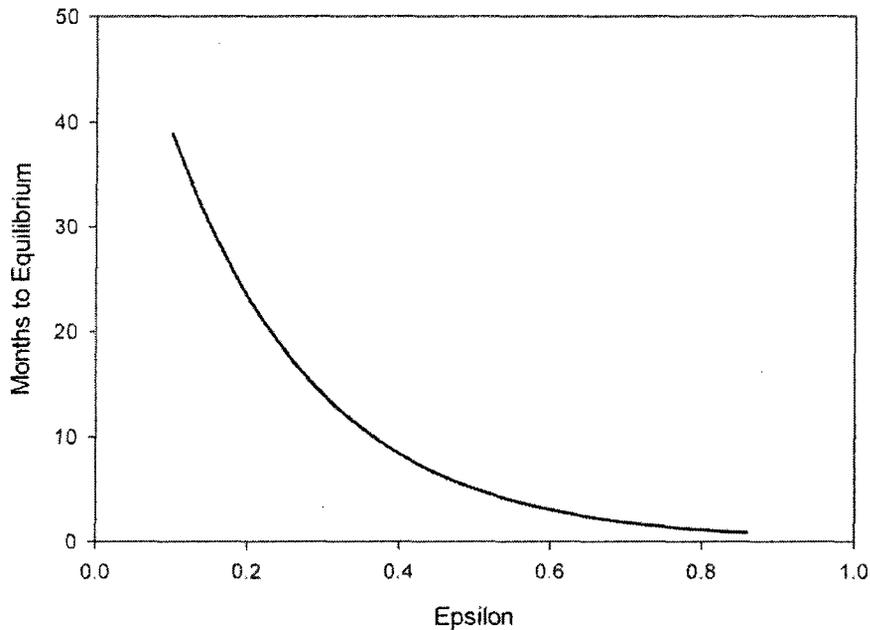


Figure 3.4. Calculated relationship between the aggregate formation rate (epsilon) and the time (months) until equilibrium is reached between the aggregated (Z_1) and non-aggregated pools (Z_2).

When evaluating the literature, there are often turnover times of C associated with macroaggregates (e.g. Beare et al., 1994b; Buyanovsky et al., 1994); and often a turnover rate, which when measured in a field or lab incubation, represent the net effect of aggregate formation and breakdown. Therefore, the aggregate breakdown rate in the model, gamma (γ), is not necessarily equal to the turnover rates reported in the literature (Puget et al., 2000; De Gryze et al., 2005). This analysis, prior to optimization, presents an empirical way to derive the maximum aggregate formation rate (when $\varepsilon = \theta = 0.21$, and $\gamma = 0.04$); because accurate estimates are unavailable.

The final optimized values of the parameters appear in Table 3.2. Microbial yield coefficients ($y_{1,3,6}$) for decomposition processes were not included in the optimization routine and were set at 0.4 (Table 3.2), which is similar to values reported in the literature and used in other SOC simulation models (Adu and Oades, 1978; Parton et al., 1987). Further, other parameters ($sorbmax$, MLC , θ , and γ) were not optimized because the internal dynamics and stability of the model are highly dependent upon these parameters (Table 3.2). We started the model with native SOC stocks generated from an off-line spin-up before optimization, so we could not alter some of the aforementioned parameters which define physical conditions directly involved in SOC dynamics during optimization. For example, we did not optimize any parameter involved in the saturation equations because a dynamic saturation constant (i.e. changing from each initial condition) would not be consistent with our definition of SOC saturation. Likewise, because the char fraction (X_C) is static in this model (i.e. not linked to other pools) we set both the pool size low and did not optimize its associated decay constant (k_C).

The optimized parameter values for the non-aggregated, mineral-associated pool (X_4) is faster than the corresponding aggregated pool (X_7). This is in agreement with observations of ^{13}C data that show carbon associated with the free mineral fractions are subject to slightly higher rates of decomposition due to increased bioavailability; the same holds true for the occluded POM (X_6) and free-POM (X_3) (Besnard et al., 1996; Gregorich et al., 1997). However, the differences are not as pronounced as the 100x slower decomposition rates used in other models when comparing occluded and free POM (e.g. van Veen and Paul, 1981).

The role of POM in aggregate stability (Oades, 1993) and nucleation processes for the promotion of new aggregate formation (Golchin et al., 1994) has been well established and confirms the underlying mechanisms of SOM stabilization. Kölbl and Kögel-Knabner (2004) suggested there is a limit to the amount of occluded POM that can be stored, even in soils with high (>50%) clay contents. The maximum contribution of I-POM carbon to macroaggregate-associated C (cIPOMmax), has an optimized value of 0.65 (Table 3.2), much higher than the 4-6% reported by Jastrow (1996). It is important to include this parameter so that POM is not transferred into aggregates without any physical limitation.

We have proposed a number of sorption and desorption processes between various pools within the model (Fig. 3.1). Specific and analogous rates from the literature are difficult to identify because the distinction between the labile and resistant mineral-associated C is not tangible at this stage and subsequent investigations into the processes that occur between them have not been elucidated. However, some of these sorption/desorption processes are in accordance with similar, proposed rates (Table 3.2). There has been much investigation into the chemical characterization of mineral associated OM, but there is not a clear chemical extraction technique to isolate a labile and resistant fraction (see review by Helfrich et al., 2007). However, numerous studies suggest that the mineral-associated OM is heterogeneous in nature (Elliott and Cambardella, 1991; Buyanovsky et al., 1994).

The optimized parameter values resulted in a RMSE of 1.2 g C kg⁻¹ soil (data not shown) across the seven selected sites (Table 3.1). We optimized across a soil carbon gradient of approximately 5 – 25 g C kg⁻¹ soil, which is representative of most arable land

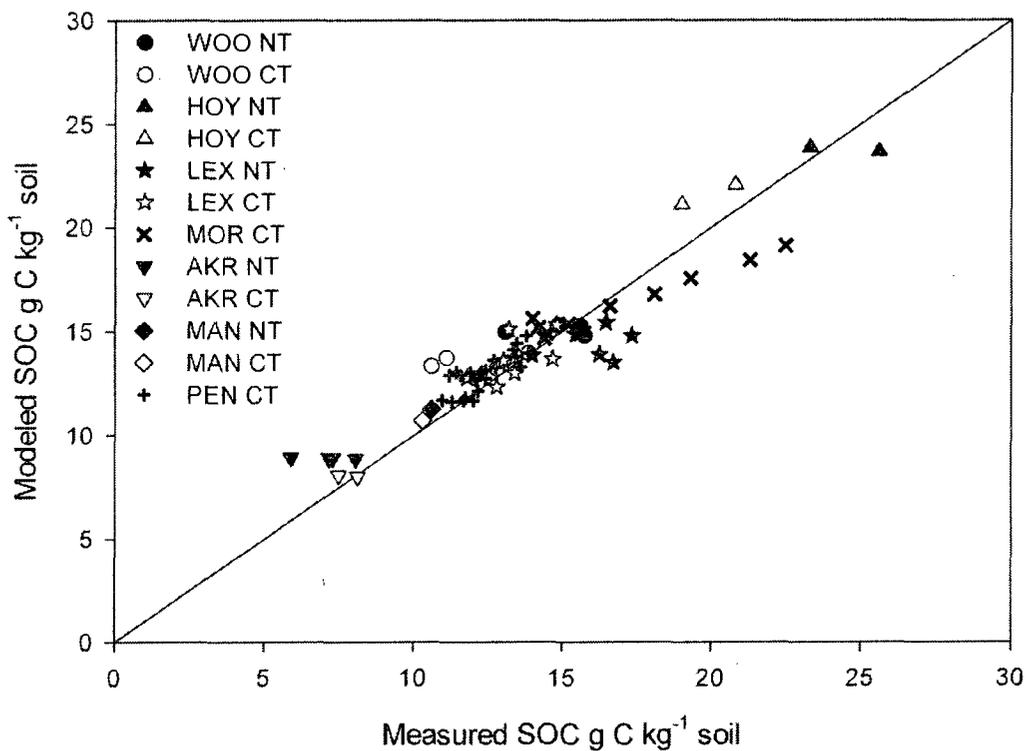


Figure 3.5. Comparison of model performance against measured soil organic carbon (SOC) values from selected long-term experiments: Akron, CO (AKR); Hoytville, OH (HOY); Wooster, OH (WOO); Lexington, KY (LEX); Urbana, IL (MOR); Manhattan, KS (MAN); Pendleton, OR (PEN). No-tillage (NT) and conventional tillage (CT) treatments have been defined for each site.

in this temperate region. There is not a strong bias in either direction (over or under prediction) across these sites and the model is distinguishing tillage treatments at the Hoytville, OH site (HOY), where SOC differences between treatments were greatest (Fig. 3.5). This was an important result of the optimization as we aimed to include tillage (or other disturbances) as a mechanism for aggregate destruction. However, without data for the individual pools, we can only speculate about the significance of the internal dynamics of the model. The model is not predicting the observed differences between

treatments (Fig. 3.5) at the Akron, CO site (AKR) but this was also one of the driest and hottest climates included in our gradient (Fig. 3.4). Perhaps the model is overly dependent upon the moisture and temperature functions described previously by Olchin et al. (2009). Similarly, NT treatments are not modeled well (Fig. 3.6) across most of the sites as temporal changes at each site are not being predicted by the model. The processes for residue incorporation (i.e. leaching of water soluble materials or translocation) may not follow simple first-order kinetics as we have assumed. At the whole soil level, the model has been optimized to an acceptable level and is now ready for verification of an independent data set, preferably with macroaggregate fractionations repeated over time.

The model appears to be under predicting the initial years at the Morrow Long-Term Experimental plots. This could be because initial SOC stocks at this site were relatively high, and native C inputs used to initialize the model were only estimates. Alternatively, this could be a consequence of an underlying assumption that bulk density is constant. This simplifying assumption propagates itself in the model when SOC stocks are calculated in conventionally tilled systems (i.e. moldboard plow) where bulk density has been shown to be sensitive to tillage management (e.g. Lal et al., 1994; Logsdon and Cambardella, 2000). Further, Malamoud et al. (2009) have included bulk density as a dynamic variable in their functional pool model. This lack of (prior) site-specific knowledge points out the importance for a model comprised of measureable pools. In the presence of appropriate data (truly unique and indicative measureable pools), the model could essentially be driven from any point of time, regardless past management.

Conclusions

With this model, we have attempted to couple SOM dynamics with aggregate formation and turnover, also including direct influence from tillage events. Few others have attempted to model both physical (aggregates) and C state variables (e.g. Malamoud et al., 2009); but this approach is necessary to truly achieve the goal of ‘modeling the measurable.’ Under the guise of an aggregate turnover model, C and soil mineral mass are indeed coupled. In addition, there may be notable changes in bulk density associated, but we make a simplifying assumption that bulk density remains constant during the simulation. This allows for an area of improvement in future endeavors of SOM modeling, whether functionally defined or not. Subsequently, we analyzed the results in concentration units, rather than soil C stocks which are more influenced by soil bulk density.

In order to better optimize the parameters in this model, a suite of data containing SOC fractions derived from an analogous fractionation scheme (Figure 3.1) is needed. Unfortunately, available data from these long-term experiments is often limited to total SOC concentrations or stocks. Even in our proposed method, we have not completely defined methods to measure every pool (i.e. X_C), and others have suggested that not every pool [in a model] can be directly measurable (see Smith et al., 2002). The initial optimization contained herein does not take full advantage of the ability to directly validate the internal dynamics of a model with measurable pools. However, designing a model from a fractionation scheme (i.e. measuring the modelable) was never our intention; which was to model the measurable.

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C H A P T E R F O U R

A Review of Functional Pool Modeling: Efforts at Modeling the Measureable

“All models are wrong but some are useful.”

Box, G. E. P. (1979). Robustness in the strategy of scientific model building.
In R. L. Launer, and G. N. Wilkinson, (eds.) Robustness in Statistics. New
York: Academic Press

Abstract

The apparent lack of correspondence between laboratory methods (i.e. measured soil organic carbon (SOC) fractions) and computer simulation efforts (i.e. modeled SOC fractions) poses a significant challenge for a better understanding of soil organic matter (SOM) dynamics. This discrepancy could possibly be resolved by conceptualization and development of models comprised of functional pools of soil organic carbon. Our objective is to review the evolution of functional pool modeling from a conceptual stage to the development of mathematical models, and propose future areas of research as they relate to functional pool modeling. The difference between conventional SOM and functional pool models is the way in which the pools are defined; the former being characterized by pools with unique kinetics. Functional pools are here defined by measureable, or isolatable, SOC fractions through physical and/or chemical fractionation methods. This concept, coined 'modeling the measurable' has motivated at least three mathematical models (SATURN, SOMA, and Struc-C) that best-fit this definition. There has also been significant activity in retro-fitting conventional SOM simulation models with functional pools. There are several proposed benefits to using models defined by functional pools, rather than kinetically-defined pools, including but not limited to the ability to directly validate the internal dynamics of the model (i.e. pool behavior). This class of models takes a more mechanistic approach by defining state variables with measureable SOM fractions and including mechanisms of SOM stabilization. This review aims to examine relevant and emerging research in SOC dynamics as they relate to the development of functional pool models. Qualitative comparisons of current functional pool models are made which reveal areas of research that should be investigated to

strengthen these models. Those areas could include the characterization of the char fraction, development of a suitable chemical fractionation to yield labile and recalcitrant SOM fractions. Then researchers must decide whether the model or the pool comes first; Elliott et al. (1996) suggested that modeling the measurable may prove more successful. Perhaps the answer lies somewhere in-between.

Introduction

Simulation models have been widely applied to the field of soil organic matter (SOM) dynamics. However, the conceptual basis used for defining the pools of these models does not align with our best conceptual models of SOM dynamics. The natural dynamics of SOM, a heterogeneous and complex matter, has been of interest since the beginning of modern soil science. Jenny (1941) and Hénin and Dupuis (1945) represent the earliest attempts at interpreting observations of SOM in relation to external factors (i.e. climate, management, etc.) into mathematical relationships that were used in early models or mathematical functions. The complex and heterogeneous nature of SOM was apparent in the beginning and following a reductionist approach, researchers tried to gain insight into the nature of SOM by isolating individual fractions that could be analyzed separately. Early characterization efforts were dominated by chemical fractionations that yielded humic acid, fulvic acid, and humin (Waksman and Stevens, 1930).

Other investigations into soil organic matter revealed the role soil structure and clay particles could have in SOM stabilization processes. Emerson (1959) explained that organic matter is protected between clay and sand particles; and that the surface area of the clay particles and these organo-mineral interactions provided the protection to microbial decomposition processes. It followed then, that the physical fractionation of soil could also characterize SOM pools representative of other stabilization processes including physical occlusion. These early and operationally-defined fractions, allowed for the characterization of the decomposability of the different SOM fractions. Concurrent to

the development of chemical and physical isolation of SOM, conceptual models of soil aggregation aimed to explain the dynamics and underlying mechanisms of stabilization and decomposition (Edwards and Bremner, 1967; Tisdall and Oades, 1982).

Observations of declining SOC stocks from intensive agriculture (Haas et al., 1957) and the spatial variability of SOM across landscapes and regions as a function of vegetation, climate, etc. (Jenny, 1941) fostered a desire to explain and predict changes in SOM content as a function of changes and perturbations to the driving variables. Simulation models allowed rapid application of hypotheses and subsequent evaluation of SOC stocks over long- or short-term time scales to be possible. However, the challenge of partitioning soil organic matter, a complex and heterogeneous substance, into pools that could be successfully modeled required theoretical model pools, often defined by their turnover times (assuming first-order decomposition kinetics) in addition to operationally-defined pools.

Early simulation models were actually much more mechanistic than more recent models, but may have included too much detail at the expense of a more parsimonious interpretation (e.g. Smith, 1979). In this early SOM model, C pools were defined by organic chemical compound classes (plant and microbial carbohydrates, polysaccharides, etc.) and the processes connecting them included specific chemical reactions (deamination, hydrolysis, etc.). The next generation of simulation models typically divided SOM into kinetically-defined pools (e.g. active, slow, and passive), which display first-order decay kinetics that differ in mean residence times, representing organic material after successive phases of decomposition or resistance to microbial degradation

(Jenkinson and Rayner, 1977; Parton et al., 1987). For thorough reviews and applications of these types of SOM models see McGill (1996), Smith et al. (1997b), and Falloon and Smith (1998).

The performance of these models was evaluated by De Willigen (1991) who noted that although some SOM models could predict long-term trends accurately, the results of short to medium term simulations were unsatisfactory. Deficiencies in predicting SOM changes across a wider range of time scales may, in part, be due to the fact that these process-based models lack some of the physical, biological, and chemical controls of SOM dynamics that could be elucidated in models more mechanistic in nature. As an alternative to defining several discrete pools, a few models represent SOM explicitly as a heterogeneous mixture defined by a reactive continuum of decreasing substrate quality (e.g. Bosatta and Agren, 1985). In a separate application of the continuous quality function, Fang et al. (2005a) identified some advantages to this approach including conceptual strength; simpler model structure with only three parameters to be estimated; and requiring only a few lab measurements of total remaining SOM and overall decomposability are needed.

Process-based models simplify the complex composition of SOM (typically into 3-5 pools) and achieve a relatively high degree of success in describing and predicting changes in total SOM as a function of land management and use across a range of climatic conditions (Smith et al., 1997a). However, the design of these models leads to some inherent shortcomings: 1) appropriate verification of the models is limited because model pools cannot be directly measured; therefore, the internal dynamics of the models cannot be tested or falsified; 2) the mechanisms relating SOC dynamics to soil physical

properties that are known to influence SOC stabilization and turnover (e.g. soil texture, clay mineralogy, soil structure) are rudimentary or lacking (Paustian, 2001).

Only recently have more mechanistic SOM models emerged that explicitly represent model pools that correspond to measureable fractions. Malamoud et al. (2009) presented Struc-C (inspired from RothC26.3), a model that includes aggregate dynamics of three size classes and a porosity submodel. Additionally, two other functional pool models, SOMA and SATURN, are being developed from the dissertation work of Sohi (2001) and (Olchin et al., 2009b, a), respectively.

Modeling the Measureable

One of the problems with modeling SOM turnover is that it has not been possible to match conceptual, kinetically-defined pools with measurable fractions – the challenge of modeling the measurable or measuring the modelable (Motavalli et al., 1994; Elliott et al., 1996). This may be due to inadequacies of physical or chemical methods to isolate fractions that are relatively ‘uniform’ (within the fraction) in terms of decomposition kinetics, since biological lability is not dependent solely on the chemical or physical forms of soil (Duxbury et al., 1989). Further, the differences in decomposition kinetics within a physically or chemically defined fraction should be less than differences among other measured fractions. In the past decade, advances in SOM characterization (from new fractionation methods) have provided new conceptual models of SOM dynamics that can be used as the foundations of new simulation models.

Conventional models have pools that are defined by their unique kinetics, whereas the new class of models is characterized by measurable or isolatable pools; now defined as 'functional pools'. These pools should be isolated by size, density or chemical methods; and yield distinct differences in biological reactivity (Sohi et al., 2001). Following this definition, proposed models should define pools that correspond to distinct, isolatable pools that are applicable across soil types and climate, rather than trying to design a new fractionation scheme to isolate pools that correspond to pools already previously defined in existing models (Elliott et al., 1996). Functionally defining model pools has been identified as an alternative (perhaps better) representation of the actual physical and chemical characteristics of SOM and the subsequent modeling of SOM dynamics should ideally be more mechanistic (Buyanovsky et al., 1994; Christensen, 1996; Balesdent et al., 2000; Arah and Gaunt, 2001).

Smith et al. (2002) stated that a measured soil organic fraction is only equivalent to a model pool when it is unique and non-composite with respect to its decomposability, which suggests that not all isolated fractions may be suitable for model fractions. For a pool to be non-composite it must contain organic matter (OM) that is homogeneous and follow a unique decomposition process, often assumed to be first-order. Likewise, if pools are not unique from one another, then there is no added benefit of having them separated into individual pools, and the most parsimonious option is often the best (Smith et al., 2002). Failing to meet these requirements may result in an unnecessary increase in model complexity from an increased number of pools and parameters, or oversimplification (combining of non-composite pools) in the model. The authors also offer criteria that can be used to determine if a measured pool is both unique and non-

composite before the model is constructed. However, a potential drawback of operationally defined fractions is that their composition may not be constant through time; therefore the particular level of reactivity would not be consistent (Sohi et al., 2005).

The development of simulation models with functional pools represents a step toward more mechanistic modeling of the various processes that control stabilization and turnover of SOM. However, the idea of using physical soil characteristics, mainly texture, as a controlling factor of a model's internal processes is not new, and has been included in several SOM models before (e.g. Parton et al., 1987; Coleman et al., 1997). In previous models the mechanisms of SOM stabilization with the mineral fraction were not explicitly included; even though this important interaction has been detailed in many SOM stabilization studies (Paustian, 1994; Elliott et al., 1996).

The apparent lack of correspondence between laboratory results and process-orientated model structure warrants new SOM models. These models might directly include the interaction between SOM and mineral surfaces – e.g. the monolayer theory (Emerson, 1977; Mayer, 1994a) – an important mechanism of SOM stabilization (Sollins, et al., 1996). The interpretation of the interaction between the mineral surfaces and SOM has profound consequences on the long-term stabilization of SOM. Given that clay particles as themselves, or as conglomerates, have a finite surface area (Feller et al., 1992; Saggar et al., 1996; Christensen, 2001); the monolayer theory defines a linear function to estimate the maximum C loading of a soil with a given clay content (Mayer, 1994a, b). By definition, the monolayer implies a single and continuous coating of OM on the clay surfaces. Others have suggested discontinuous and layered interactions

observed by transmission electron microscopy and a conceptual model defined by organic functional groups of SOM compounds by Chenu and Plante (2006) and Kleber et al. (2007), respectively.

Though it is widely accepted that soil structure (i.e. aggregation) provides some level of physical protection and therefore eventually promoting stabilization of SOC (Sollins et al., 1996; Baldock et al., 2004); most simulation models also neglect to include, or oversimplify this mechanism and could benefit from the inclusion of aggregate dynamics and distributions (Elliott et al., 1996; Six et al., 2002). Interestingly, Poirier et al. (2005) pointed out that the earliest version of the RothC model (Jenkinson and Rayner, 1977) included a physically protected pool, but because there was no apparent means to experimentally quantify this pool it was eventually phased out. Later, the model of van Veen and Paul (1981) included the concept of physical protection for some of their SOM pools, and began to consider that tillage disrupted the protection capacity. Their interpretation of long-term data confirmed that 50-60% of SOM was protected, subject to slower decomposition rates, and influenced by the degree of aggregation and clay content; this represented a significant step towards a more mechanistic approach. Similarly, the 'passive' pool in Century was originally described as "chemically recalcitrant pool that may also be physically protected..." (Parton et al., 1987).

Perhaps the first discussion of the weak correlation between measurable SOM fractions and simulation/conceptual model pools was from Duxbury et al. (1989) who identified this apparent knowledge gap as a "research imperative." Furthermore, they pointed out that the conceptual definitions of SOM pools (e.g. the 'inert' pool) need to be

refined in order to possibly align with measureable fractions, either chemical or physical. Paustian (1994) concurred, adding this disconnect created a major constraint for process-orientated models and that future models with experimentally determined OM pools should explicitly include soil structure dynamics. The idea of including soil structure dynamics, presumably aggregates of varying size classes, is a straightforward attempt at connecting a measureable SOM fraction with model pools. This approach clearly transitions from traditional, process-orientated modeling to a more mechanistic model, as others have suggested (Hassink, 1995; Christensen, 1996).

In the absence of measurable pools, comparisons for validation or verification purposes against system-level output (i.e. total SOC stocks) mask and cannot accurately predict the process-level dynamics driving the model (Sohi et al., 2001). In addition to the traditional convention of modeling and comparing total SOC stocks, a model with measureable pools would allow the internal dynamics of the model to be further tested and could reveal how the contributory SOC pools are changing with land use and management, environmental factors, and/or time (Christensen, 1996; Paustian, 2001). Further, Skjemstad et al. (2004) postulated that the correct prediction of the changing total SOC levels, as well as the pool structure over time, could act as an internal verification in the RothC model. The question then arose whether to ‘model the measureable’ or ‘measure the modelable.’ Researchers must decide whether the model or the pool comes first; Elliott et al. (1996) suggested that modeling the measureable may prove more successful; perhaps the answer lies somewhere in-between.

Relevant Current Research Efforts

Recently, terrestrial carbon sequestration has been identified as a potential greenhouse gas mitigation strategy (Paustian et al., 1997). However, the assumption of linear relationship between SOC stocks with C inputs may not be safe, and alternative dynamics would have severe implications on the long-term dynamics of SOC. Soil organic carbon saturation can be defined as the point where a soil is incapable of accumulating and stabilizing more C (Six et al. 2002). The inclusion of potential SOC saturation in simulation models is warranted from the implications this phenomenon could have on soil carbon sequestration efforts, often evaluated through simulation models. For a thorough review and evidence of the saturation concept see Six et al. (2002), West and Six (2007), and Stewart et al. (2007). While this section does not intend to be a complete review of the SOC saturation, we aim to promote for its inclusion in SOM models because of its inherent association with isolatable fractions, namely the mineral fraction ($<53 \mu\text{m}$). Notably, other functional pool models which initially lacked SOC saturation dynamics suggested this is an area for improvement within their own model development (Malamoud et al., 2009).

The concept of SOC saturation is difficult to imagine because it is often not observable over moderate time scales (decades) with relatively low inputs from modern agriculture. Early discussions of a 'protective capacity' suggested a linear relationship between protected C within the clay sized fraction, only limited by the amount of clay (Hassink, 1996); the difference between a given organic C content and the protective capacity was then defined as the saturation deficit. Further work built upon this linear relationship, but extended the protective capacity to the whole soil (Hassink, 1997;

Hassink and Whitmore, 1997). However, this was not whole soil saturation in the sense that they suggested further additions of organic matter would result in an accumulation of the light- and intermediate organic fractions (Hassink et al., 1997).

It follows then, that SOC levels in excess of a protective capacity (saturation) could be defined by an equilibrium between C inputs and decomposition processes for a given land use and site specific conditions. If land use were to change, a new equilibrium could be reached, but the defined saturation level would not change (West and Six, 2007). This was supported by Stewart et al. (2007) who evaluated whole soil organic C levels across a wide variety of C inputs (not clay content) from long-term field experiments assumed to be at, or approaching equilibrium. They compared three simple models: 1) a linear model with no saturation; 2) a one-pool, whole-soil C saturation model; 3) and a two-pool mixed model with C saturation of a single C pool, but not the whole soil. The one-pool model with whole-soil C saturation had the best fit across a suite of sites.

Gulde et al. (2008) investigated if and how SOC fractions demonstrated saturation. They showed that the proportion of coarse particulate organic matter ($<2.3 \text{ g cm}^{-3}$) increased across all C inputs while the C content of mineral fraction ($<53 \text{ }\mu\text{m}$) making up macroaggregates ($>250 \text{ }\mu\text{m}$) did not change significantly with increasing manure application. This supported the hypothesis that physically protected C pools are subject to saturation, while the particulate (non-mineral associated) organic matter was not. The functional pool model described by Olchin et al. (2009b; a) includes saturation terms in the mineral fractions. This represents one of the first major efforts to explicitly include the concept and subsequent behavior of SOC saturation in a SOM model.

Challenges

Pools from Fractionation

It is unlikely to expect a universal fractionation scheme from the research community and functional pool models will vary accordingly. Of the many types of extraction procedures, each has its own inherent strengths and weaknesses, with each capable of isolating unique fractions that differ in decay kinetics (Olk and Gregorich, 2006). For example, chemical extractions alone do not provide information on the relation between the extracted organic matter and its physical location within the soil matrix; and physical fractionations are less successful in isolating fractions derived from microbial metabolism, which can be strongly affected by cultivation practices (Six et al., 2000). Physical separation may also reveal SOM fractions that are more sensitive to cultivation than just examining total organic C or N stocks (Cambardella and Elliott, 1992). Building off of current conceptual models of soil aggregation, De Gryze et al., (2006) stated that soil aggregates could serve as ideal units for reproducing the processes of physical protection and saturation, claiming SOM models could benefit greatly by including the concepts of aggregate turnover and their distribution. Previously, Paustian (1994) had suggested that future model and experimental development should include relating soil structure to organic matter and nutrient dynamics in an effort to achieve closer correspondence between theoretical constructs of SOM and analytically defined SOM pools. Physically defined fractions may eventually have their place in modeling, but consideration should be given to the extent of fractionation. Chenu and Plante (2006) suggested that using density separations within the clay-sized fraction is not justified because of the continuum of materials associated with this fraction. Others have

suggested that functional pools should be defined by stabilization mechanisms rather than specific fractionation techniques (von Lützow et al., 2006; 2007).

Alternatively, researchers are focusing efforts to identify potential fractionation schemes that may yield pools suitable for modeling. Parton et al. (1996) noted the apparent lack of physical or chemical methods to directly isolate OM pools with decomposition kinetics similar to those in conventional models, posed a significant challenge in studies of SOM dynamics. Similarly, Smith et al. (2002) suggested that isolated pools are often heterogeneous in decomposability, unlike the conventional, kinetically-defined model pools. They also suggested that chemical and physical fractionation methods did not isolate SOM compounds with uniform kinetic behavior or were difficult to link with kinetically-defined pools, respectively. Nichols and Wright (2006) isolated eight operationally defined pools from sequential physical and chemical separation techniques, including particulate organic matter (POM), humic and fulvic acids, glomalin, and others. They pointed out that conventional extractions often yielded heterogeneous fractions and were not stringent enough to produce chemically unique pools, specifically within the POM fraction. A common contamination was glomalin-derived protein found in humic acid fractions when glomalin was not removed first.

Sohi et al. (2001) outlined a procedure for isolating measurable pools and found that physical separation produced size fractions that contained a mixture of organic compounds because complete separation of POM from the mineral fraction had not occurred. However, fractions with different densities displayed distinct differences in biological reactivity which could reflect the chemical properties. They concluded that density fractions (physical fractionation) provide a sound basis for developing a

functional pool model. Though the fractionation schemes are slightly different between Sohi et al. (2001) and Nichols and Wright (2006), it highlights the importance of consistent fractionation techniques as they are inherently designed to isolate specific SOM pools that are not necessarily interchangeable.

In an application of the previous fractionation scheme, Sohi et al. (2005) found certain, significant chemical differences across a wide range of geographic locations between free soil organic matter (FR-SOM) and intra-aggregate POM (IA-SOM), both with densities less than 1.80 g cm^{-3} . Therefore, they postulated that these two pools should be widely applicable in simulation models of SOM across different locations. Poirier et al. (2005) subjected these two SOM fractions and the residual heavy fraction (mineral associated, M-SOM) to a thorough suite of chemical analyses and found a decreasing reactivity in the order of FR-SOM > IA-SOM > M-SOM; further supporting the data that these pools represent suitable fractions with unique decomposition rates.

Mineral Pools

The complex interactions that occur between the mineral surface and soil organic matter have been crucial (albeit understated) to modeling efforts for quite some time, as previously outlined. Whether this pool, or group of pools as it may be, is subject to saturation or represents a limitless sink for SOC storage is not the aim of this section (see above section), but rather to discuss how to represent such a complex pool. Ideally, a modeled fraction would represent a group of organic compounds which are both unique and non-composite in decomposition kinetics (Smith et al., 2002). A challenge then arises because much research has shown that organic matter associated with the mineral phase

is just the opposite (Tiessen and Stewart, 1983; Balesdent et al., 1988; Buyanovsky et al., 1994; Kleber et al., 2007).

A realistic approach is to use fractionation methods as a means to isolate functional pools. Chemical agents are commonly used to remove a proportion of the mineral-associated OM, and by measuring the difference one could calculate the size of the pools. Recent research has shown that chemical treatments often leave a fraction that is not indicative of land use history (Chenu and Plante, 2006); an older and chemically resistant fraction (Zimmermann et al., 2007a); and a fraction that is independent of the initial amount of OM in the mineral phase (Helfrich et al., 2007). Despite some discrepancies among chemical agents, a consistent quantity and quality of OM across sites and land-uses suggests that stabilization of OM in the mineral phase may not be controlled by external factors, but rather from the mineral-phase itself. However, investigations into the surface condition (specific surface area) before and after chemical digestions are limited. It follows that the concept of SOC saturation in the mineral phase is important when considering SOM dynamics (Hassink and Whitmore, 1997; Stewart et al., 2007).

Alternatively, the presumed heterogeneous nature of, and complex interaction between OM and the mineral surface could be described by at least two kinetically-defined pools (Balesdent et al., 1987; Puget et al., 2000; Chenu and Plante, 2006). Within the mineral-phase, the ratio between a chemical-resistant and total mineral OC could serve as a proxy for partitioning these two pools, perhaps making a fractionation process unnecessary. Chemical fractionation of the mineral-associated OM is not consistent (discussed in previous section) and therefore not worthwhile when developing a new

model because the proportions of a labile and recalcitrant fraction would have to be estimated when the fractionated data did not align with the model structure. While this may not completely satisfy the conditions for a functional pool, it is certainly a step toward a more functional representation of SOM pools.

Inert Pool

The fraction of SOC that has been defined as ‘inert’ in simulation models (Jenkinson, 1990); or as charcoal (Skjemstad et al., 2002); or simply as ‘black carbon’ (Schmidt et al., 2001); is also important to functional pool modeling. However, this pool has remained in a conceptual stage and requires a consistent method for isolation and measurement before it should be fully linked to other pools in simulation models. The importance of this fraction to SOC storage is well founded as turnover times have been estimated from hundreds to thousands of years (Skjemstad et al., 1996; Hammes et al., 2008). Despite its relative abundance and significance, this SOM fraction has also been underrepresented in current SOM models. In the Rothamsted carbon model, the conception of this pool rose from radiocarbon data and chemical fractionations that indicated soil OM fractions of different ages (Jenkinson and Rayner, 1977). Later, the inert fraction was justified because simulations without it greatly underestimated the measured age of SOC, and inclusion did not significantly alter the total soil C level. It seems that by matching this conceptual pool with a measureable pool, as suggested by Falloon et al. (1998), supports its inclusion in simulation models. Helfrich et al. (2007) suggested that SOM modeling efforts could be greatly improved by isolating a stable SOC fraction analogous to this pool. The challenge, again, is finding a suitable

fractionation procedure that represents the conceptually ‘inert,’ or better stated, ‘refractory’ pool; because even this highly recalcitrant fraction is subject to some degree of decomposition.

Retrofitting

Some model developers have considered restructuring or calibrating current SOM models with measurable SOC pools, even though this strategy may require “radical” changes to current SOM structure (Malamoud et al., 2009). In calibrating the RothC model with measurable pools (POM, charcoal-carbon, and humic acid), Skjemstad et al. (2004) noted that 1) the versatility of a model could be greatly improved if the SOC pools could be directly measured; 2) the model could be initialized at any point in the landscape without the necessity for historical data; and 3) the correct prediction of the changing total SOC levels as well as the pool structure over time would act as an internal verification. They also found good agreement between measured and modeled total organic carbon and pool data across two very different environments, three soil types, and three distinctly different crop rotations. Another attempt at retro-fitting RothC utilized a combination of physical and chemical fractionation techniques. Zimmerman et al. (2007b) combined functional pools and then split them (according to modeled equilibrium conditions) to make comparisons between conceptual pools and isolated fractions. Further, at least two other sources have identified fractionation schemes that isolate measureable pools corresponding to the pools in RothC (Falloon et al., 1998; Shirato and Yokozawa, 2006). While these efforts have highlighted the robustness and identified measurable pools that correlate well with the conceptual pools of RothC, it

seems they are attempting to model the measurable by identifying fractions (both chemical and physical) that related well to RothC. Certainly this approach is valid when future simulations are compared to the identified measured fractions, but any statistical comparisons between a functional pool model (as defined earlier) and a conventional model are lacking.

Likewise, Magid et al. (1997), endeavored to ‘measure the modelable’ and vice versa to test organic matter dynamics in the DAISY model by using measured field data (e.g., soil microbial biomass, CO₂ evolution, C:N ratios of residues) to parameterize the model and then simulating observed data for the following year’s data. However, this approach was not directly using measurable pools to simulate SOC dynamics, but rather calibrating parameter values with measured data to enhance the model’s performance, albeit the model was still comprised of kinetically-defined pools.

Functional Pool Models

Recently, a new conceptual SOM model (Fig. 4.1) based on measurable SOM pools was proposed and uses the aggregate turnover concept to explain the physical protection of soil C within aggregates (Six et al., 2002). Their (conceptual) functional pool model explicitly includes mechanisms of physical protection of organic matter associated with aggregate formation and mineral-associated C saturation. Similarly, von Lützow (2008) proposed another conceptual model (Fig. 4.2) that shows similarities between established conceptual model pools to functional soil OM fractions. For each conceptual model (Six et al., 2002; von Lützow et al., 2008), the connections between the

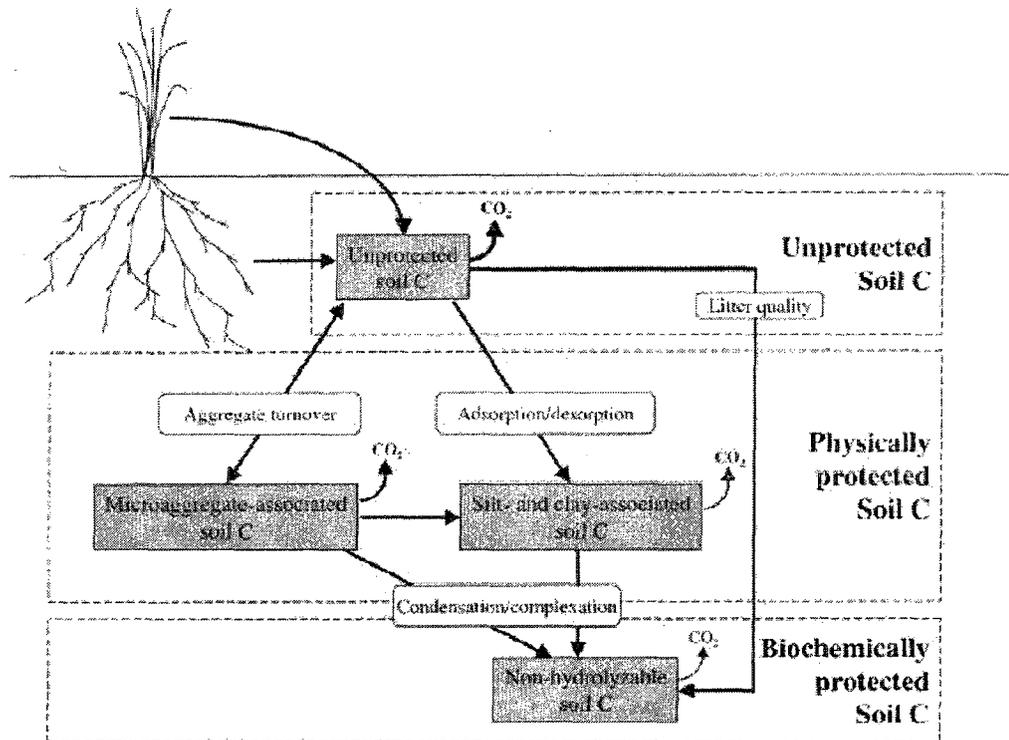


Figure 4.1. Conceptual model of soil organic matter (SOM) dynamics with measurable pools adapted from Six et al. (2002). Soil organic matter dynamics are determined by processes of aggregate formation/degradation, adsorption/desorption of organic matter with the mineral phase, condensation/complexation, and the litter quality plant residues.

the functional SOM fractions are the conventional stabilization mechanisms proposed by Sollins et al. (1996). Conceptual models like these can be used as foundations, or guiding principles, for the development of new functional pool models; just as early understandings of decomposition kinetics served as a basis for conventional SOM models. Functional pool models are the result of taking a more mechanistic approach to SOM modeling.

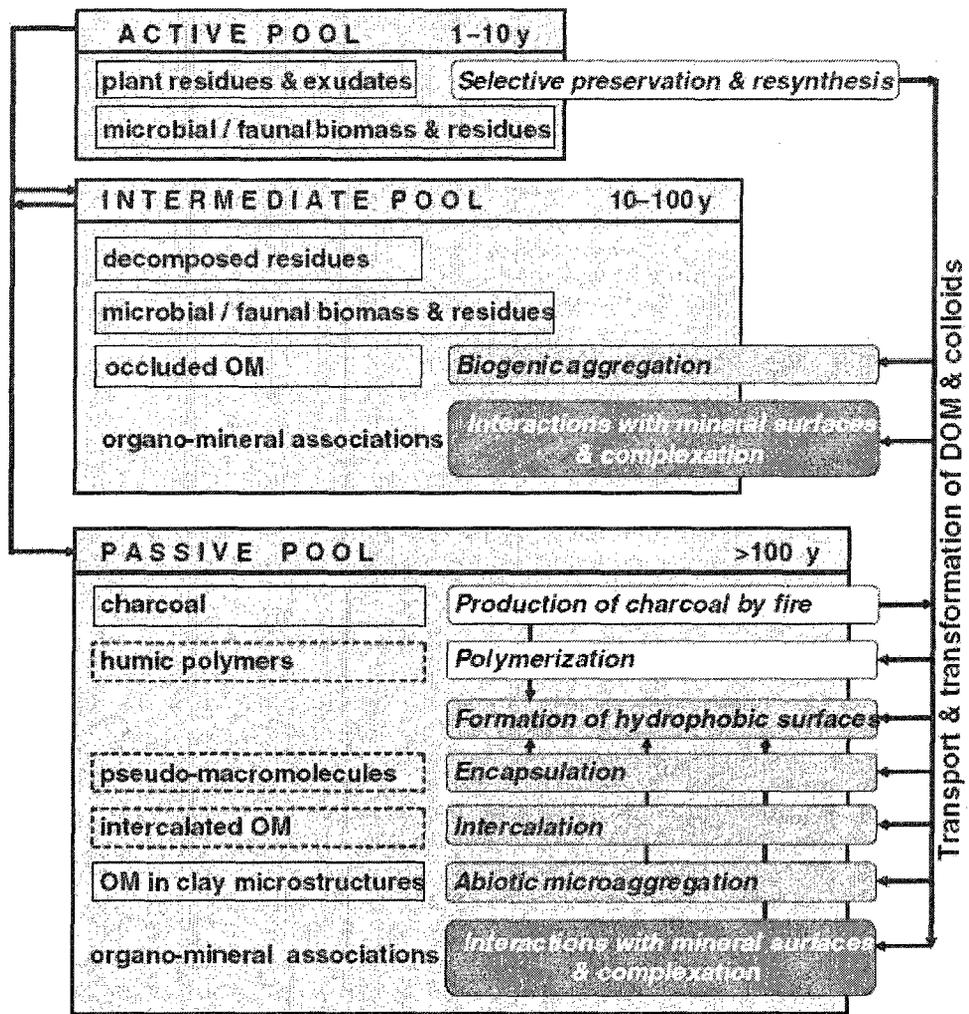


Figure 4.2. Conceptual model of organic-matter (OM) stabilization adapted from von Lütow et al. (2008). Three process groups of stabilization mechanisms are shown: □ = primary and secondary recalcitrance, ◻ = spatial inaccessibility, ■ = organo-mineral interactions. Pools within broken lines indicate postulated pools; their existence has not been verified by direct measurements.

SATURN

The SATURN model (Table 4.1, Fig. 4.3), described in detail by Olchin et al. (2009b; 2009a), includes both soil aggregate dynamics and the potential for SOC saturation. This model also integrates tillage events, clay mineralogy, and residue litter inputs; allowing us to qualitatively and quantitatively examine the hypotheses developed from and included within the conceptual model of Six et al. (2002). Briefly, this model is comprised of nine SOC pools which are coupled to other state variables for ‘aggregated’ and ‘non-aggregated’ soil proportions (Table 4.1). This model proposes the use of both chemical and physical fractionation techniques to isolate functional SOM pools. Even so, residue inputs are still split into kinetically-defined pools using a plant residue quality index (Olchin et al., 2009a). Likewise, within the mineral fraction (where saturation occurs), organic C is partitioned into a labile and recalcitrant pool, which could be divided and measured using any one of the many chemical fractionation methods being evaluated in the literature (see Helfrich et al., 2007). There is evidence supporting the heterogeneous decomposability of mineral-associated C (Tiessen and Stewart, 1983; Balesdent et al., 1988); and current chemical separation techniques that can yield two fractions (Zimmermann et al., 2007a). If valuable information can be gained by splitting the mineral associated C fractions then it should be done at the expense of parsimony. In this instance, a mechanism for organic matter stabilization (afforded by microaggregates) is expressed as a unique transfer between the labile and recalcitrant mineral-C only within macroaggregates instead of including more pools for microaggregate dynamics. At this stage only an initial parameterization of SATURN has been done (Olchin et al.,

Table 4.1. A collection of current functional pool models and their vital characteristics.

	SATURN (Olchin et al., 2009b, a)	SOMA (Sohi, 2001) (SOMA, 2009)	Struc-C (Malamoud et al., 2009)
Key citation			
Fractionation technique	Chemical Physical	Physical	Physical
How are pools defined?	Functional Kinetic	Functional	Functional Kinetic
Sub-models	SOC ¹ dynamics Macroaggregates	C, N, ¹³ C, ¹⁵ N	SOC dynamics Aggregates Porosity
Contributing SOC Pools	Structural residue (> 2mm) Metabolic residue Free POM Intra-aggregate POM Free-labile mineral-associated Free-recalcitrant mineral associated Aggregated labile mineral-associated Aggregated recalcitrant mineral-associated Char	Intra-aggregate POM Free POM Microbial Soluble Heavy fraction Gaseous	Decomposable plant material Resistant plant material Primary mineral complexes Microaggregates (< 53µm) Macroaggregates (> 250 µm) Non-Complexed Organic C
Fundamental Concepts	Potential SOC saturation Aggregate turnover Organo-mineral interaction	Organo-mineral interaction Coupled C-N dynamics	Aggregate turnover Organo-mineral interaction
Aggregate Formation	f _{clay} and oxide content, POM)	N/A	f _{clay} content, SOC)
Rate Modifiers	Temperature Moisture	Temperature Moisture	Temperature Soil Moisture Deficit Soil Cover

¹Particulate organic matter (POM); Soil organic carbon (SOC)

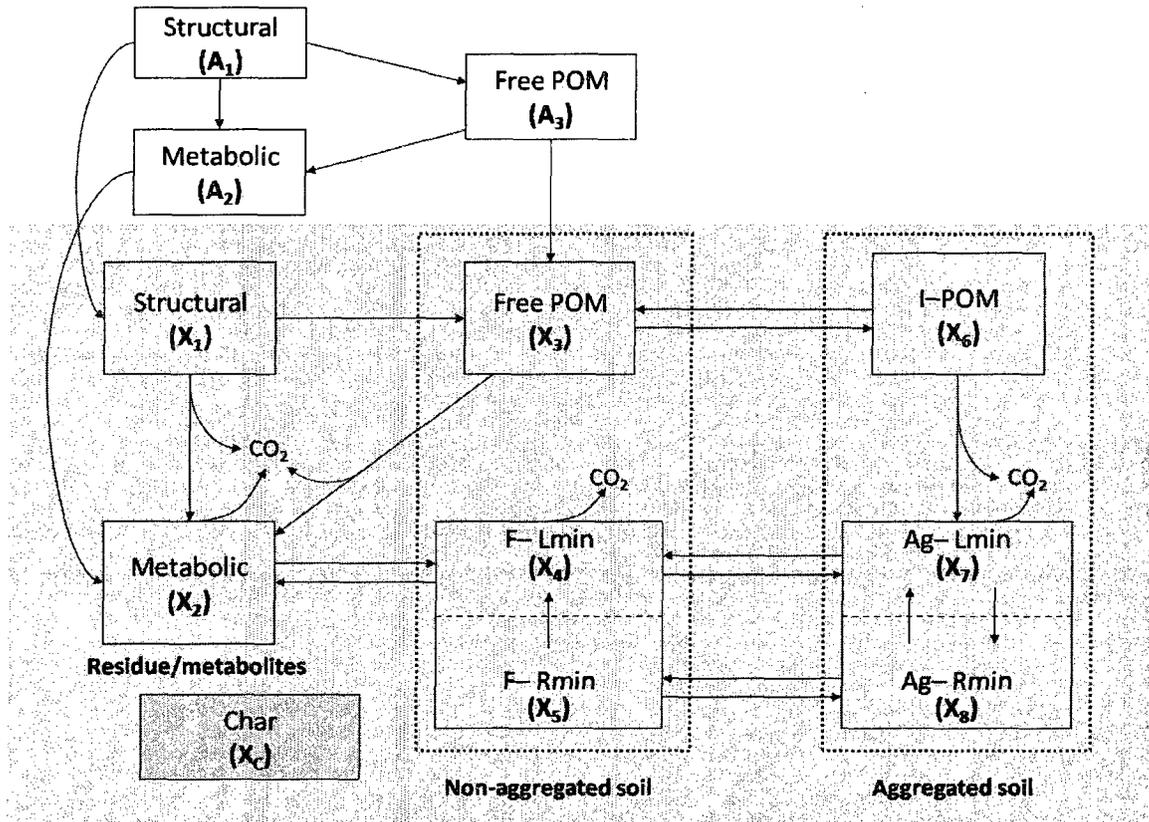


Figure 4.3. Conceptual depiction of the functional pool model, SATURN. Shaded area denotes belowground pools (X_i , X_C), and the associated aboveground pools (A_i). Free-particulate organic matter (Free POM; X_3) is distinguished from intra-aggregate organic matter (I-POM; X_6) by the dotted lines. Similarly, two distinctions are made within the mineral associated C: 1) non-aggregated mineral C is split into labile (F-Lmin, X_4) and recalcitrant (F-Rmin, X_5) fractions; 2) aggregated mineral C is likewise split into labile (Ag-Lmin, X_7) and recalcitrant (Ag-Rmin, X_8).

2009b). The added benefits of functional pool modeling include additional comparisons between measured SOM fractions with model outputs – at greater detail than total SOC stocks.

SOMA

Taking a slightly different approach, Sohi (2001) defined a model (Fig. 4.4) with functional pools by first identifying suitable fractions for modeling. In comparing fractionation techniques, they suggested that size fractions were chemically similar but that density fractions displayed distinct differences in biological reactivity. These differences reflected chemical properties making physically isolated fractions more useful in modeling measurable pools than the more classical chemical fractionation approaches. If Elliott et al. (1996) suggested to 'model the measurable' then this approach can be called 'measuring the modelable.' Their model represents a reductionist's approach as the model is limited to five conventional SOM fractions defined by the most fundamental components of soil properties (e.g. organo-mineral complexes, POM fractions, and soluble C). In addition to modeling SOC dynamics, Sohi (2001) also pointed out that a functional pool model should be able to model N dynamics as well; subsequently SOMA includes the added capacity to model C, N, ^{13}C , and ^{15}N . At this time, this model has only been parameterized and not exposed to other independent data sets. The inclusion of N to this model differentiates it from other functional pool models and also adds more detail and controls on SOM decomposition, often an N-limited process. Briefly, the model is comprised of six pools (Table 4.1, Fig. 4.5) and represents a reductionist approach to defining model pools. Here soil samples are subject to a combined size and density fractionation scheme that yields the organo-mineral and both free and intra-aggregate POM fractions (Sohi et al., 2001).

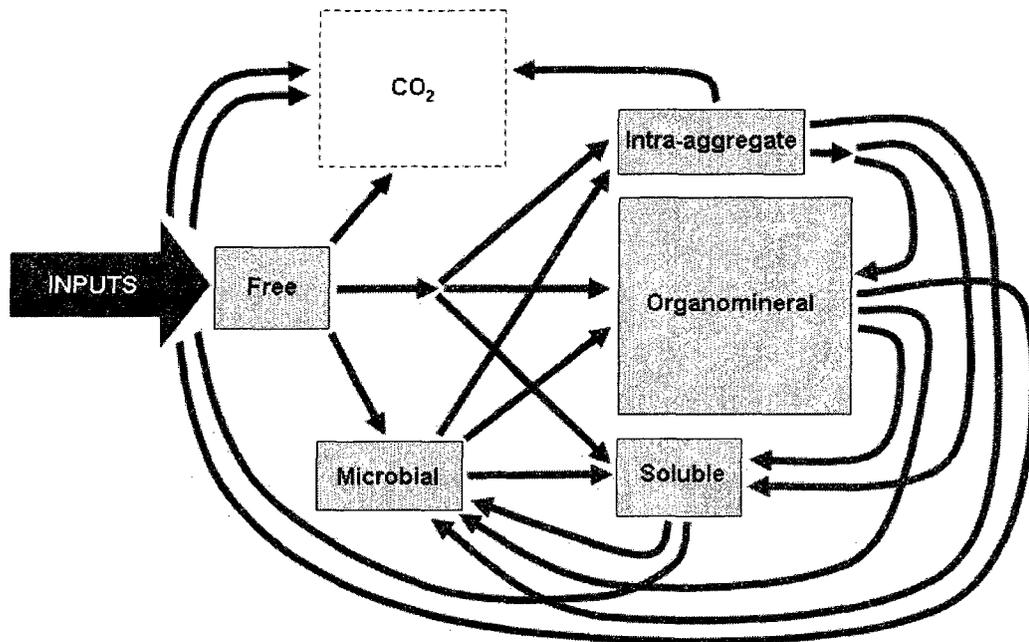


Figure 4.4. Model diagram of SOMA; adapted from SOMA (2009). Here the model pools (as in Table 4.1) are defined by the outlined boxes with arrows representing the transfers of C between pools. Soil organic matter is defined here as the sum of the free particulate organic matter fraction (Free), intra-aggregate particulate organic matter (Intra-aggregate), the microbial fraction, a ‘Soluble’ fraction, and the mineral associated organic matter (Organomineral).

Struc-C

In an attempt to describe connection between the biology, chemistry, and physics of aggregate formation, Malamoud et al. (2009) presented a model (Fig. 4.5) comprised of three submodels which are linked together by six pools describing porosity, aggregate structure, and SOM dynamics. Having drawn inspiration from the RothC model, their model (aptly named Struc-C) contains SOC pools defined by increasing levels of physical protection from decomposition afforded by interactions with minerals (Table 4.1).

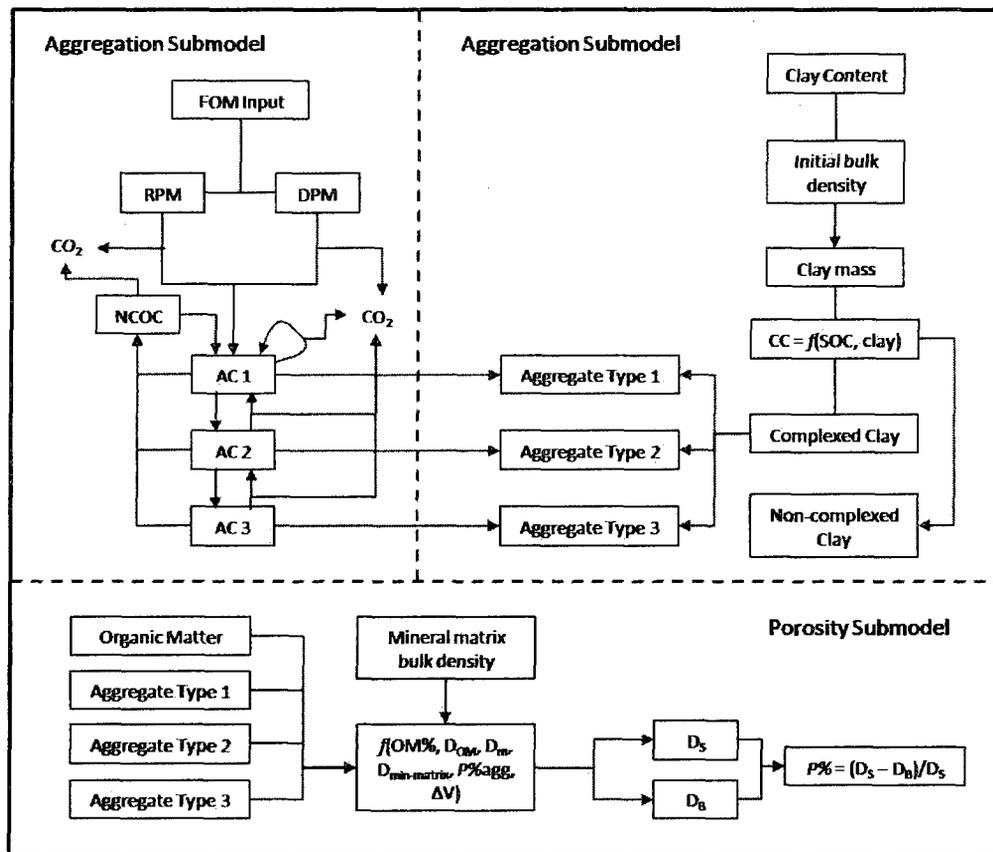


Figure 4.5. Diagram of the Struc-C model, adapted from Malamoud (2009). FOM = fresh organic matter; RPM = resistant plant material; DPM = decomposable plant material; NCOC = non-complexed organic carbon; SOC = soil organic carbon; AC_i = carbon associated with aggregate class (1-3); CC = complexed clay; OM = organic matter; D_{OM} = particle density of organic matter; D_M = particle density of the mineral phase; D_s = particle density of the whole soil; D_b = bulk density of the whole soil; D_{min-matrix} = density of the mineral fraction; P%_{agg} = aggregate induced porosity; V = soil volume; P% = porosity.

Similarly to SATURN, this model also splits plant residues into two pools of contrasting decomposability, a strategy that has been the practice in conventional models. This model attempts to describe aggregate dynamics for three size classes as a function of clay and SOC contents, but noted that oxide presence and mineralogy are important, though omitted, mechanisms (Malamoud et al., 2009). Initial comparisons have been

made between Struc-C and RothC for two different sites, but as is often the case, data sets of SOC fractions comparable to model pools are lacking and the internal dynamics of the model remain untested.

Olchin et al. (2009a) showed how a physically defined characteristic of soil (e.g. saturation) should not be dynamic in time, but is rather a constant parameter in dynamic equations for model pools. In this example, aggregated soil (>250 μm) is defined by (Z_2) and non-aggregated soil as (Z_1). Their respective state equations (Equations 1 and 2)

$$\frac{dZ_1}{dt} = MT(-\varepsilon Z_1 + \gamma Z_2) \quad (1)$$

$$\frac{dZ_2}{dt} = MT(\varepsilon Z_1 - \gamma Z_2) \quad (2)$$

$$SD_4 = 1 - \frac{x_4}{(Z_1 \times SL)} \quad (3)$$

represent a simple way to express aggregate formation (ε) and turnover (γ). A saturation deficit (SD_i) was defined (Equation 3) in order to couple the saturation constant (e.g. SL) with the aggregation state (e.g. Z_i) for any time step it. The saturation deficit ensures that the sums of analogous organo-mineral pools do not exceed the saturation constant (Olchin et al., 2009b). This definition allows aggregation changes to occur along with the distribution of C between the two aggregation states without changing the saturation parameter.

In the Struc-C model, Malamoud et al. (2009) not only describes changes in aggregation but porosity as well (Fig. 4.5). Porosity, bulk density, and particle density are all calculated from the distribution of three aggregate size classes. To couple C complexation with mass transfers between aggregates they use an empirical model from

Dexter et al. (2008). Briefly, an aggregate can be defined by a simple function of SOC and clay content, with a ratio of clay particles to SOC ‘particles’ of 8-11:1. Thus, changes in aggregation also result in direct changes of organo-mineral complexes between aggregate pools.

These two strategies represent opposing assumptions each with their own consequences. In the later example, bulk density is dynamic, whereas in the case of SATURN bulk density is assumed to be constant. More importantly, these two efforts represent a shift in model conceptualization where SOC dynamics are coupled to physical processes. However, the model from Sohi (2001) disregards the aggregation state of the soil and reduces soil to primary components that are then modeled; thus eliminating the need to couple SOC dynamics with changes in soil aggregation.

Added Value

If isolated fractions of SOC, whether from chemical extraction or physical separation, are shown to be both reliable and modelable pools across a variety of environments and land use, then functional pool models could prove to be a valuable research tool. Ideal pools in these models would be good indicators of past land use (i.e. those with long residence times) as well as representing fractions with short residence times that are sensitive to present management. In conventional models (with non-measurable pools) the user has to recreate the past history in order to initialize the pools. There would be no need to ‘spin-up’ functional pool models for initialization because the measured values of the state variables (pools) are indications of the current state of the system; and could then be used as a starting point for further simulations. Conventional

simulation models start at simulated equilibrium point and then proceed with simulations to compare against modeled data. The ability to ‘plug-and-play,’ minimizes the need for thorough background information on land use history and even prior C inputs because the pools themselves provide this information.

Perhaps the most important added benefit would be the ability to directly measure pool sizes for validation and verification purposes. Soil organic matter cannot be reliably fractionated into homogenous materials with unique decay constants (Gaunt et al., 2000); therefore fractionation schemes that serve as the basis for functional pool models are designed so that the differences within pools are less than the differences among the other pools. Direct measurements can be made to verify the components (i.e. model pools) of total SOC stocks, a common metric for the evaluation of SOM performance. This allows for greater insight into the proposed mechanisms of SOM stabilization as well as the dynamic nature of SOC that cannot be elucidated when only measuring (and modeling) total SOC stocks.

Conclusions and Future Endeavors

A challenge for functional pool models is the coupled interaction between SOC and soil minerals if physical fractionation schemes are applied. By definition, physically-defined pools are coupled to C dynamics – a consequence of the organo-mineral interaction. For dimensional congruity, the units of C are often expressed as stocks within a model and a pedotransfer function could then be used to convert model-generated outputs to desired units. In the simulation models described above, there have been two strategies to couple C stocks with changes in soil aggregation (i.e. soil mass).

There are many caveats of environmental modeling – one being that models are, at best, a simplification of reality that is used to gain insight and understanding of a particular system. The work from Elliott et al. (1996) raised a serious question – whether to model the measurable or measure the modelable – with either option, an important link between tangible SOC pools with model pools was made. They also suggested that direct comparisons between field/lab measurements with model pools is a way we can evaluate how well our models are describing reality. Therefore, functional pool models are (in part) an attempt to develop models that can be subject to a higher level of scrutiny. Elliott et al. (1996) went so far as to say that:

“Models will become the powerful tools we hope them to be only if we continue to interplay the development of models and their experimental and methodological counterparts.”

Our challenge is to then continue developing conceptual models of SOC dynamics; working on lab methodologies that can fractionate meaningful SOC pools; and finally evaluating them with simulation models comprised of measurable pools.

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C ONCLUSION

A thorough understanding of soil organic matter (SOM) dynamics is necessary before soils can be utilized for sustained agriculture production as well as potential greenhouse gas mitigation through terrestrial carbon sequestration. Emerging research, such as saturation dynamics, has highlighted important concepts relative to the long-term dynamics of soil organic carbon (SOC). The relationship between C stocks and C inputs from crop residues has typically been considered linear (Duiker and Lal, 1999; Huggins et al., 1998; West and Six 2007). However, recent research has shown that with increasing C inputs, there is a limit to the amount of C that is stabilized by the mineral fraction (Hassink et al., 1997; Stewart et al., 2007). The conventional SOM models have been useful for applying our understandings of soil organic matter dynamics to hypothetical or observed management scenarios but lack these emerging concepts.

This modeling effort represents a significant departure from the current paradigm represented by most SOM models (e.g. see reviews of SOM models in McGill 1996, Smith et al. 1997). Conventional models have typically been defined by kinetically-defined pools whereas the proposed model herein is comprised of mostly measurable pools. While we build upon the knowledge and experience derived from working with conventional models, particularly the Century model (Parton et al. 1987), this model incorporates three key features: 1) it incorporates the concept of pool saturation and saturation mechanisms; 2) the pools (state variables) are defined on the basis of analytically measurable soil organic carbon (SOC) fractions; and 3) aggregate dynamics are explicitly expressed.

The goal of modeling soil C fractions that more closely correspond to analytically measured fractions has been articulated by several authors over the past few years (e.g.

Elliott et al. 1996, Christensen 1996, Sohi 2001), and mathematical models are now emerging (Sohi 2001; Olchin et al., 2009a, b; Malamoud et al. 2009). Functional pool models may provide a more robust interpretation of organic matter behavior in soil than is provided by simple kinetically-defined SOM pools. Further, distribution of C among the pools can be directly estimated from measured data and the ‘internal dynamics’ of SOC transformations can then be validated, rather than estimating pool distribution at the onset of simulation.

Functional pool models lend themselves to easier validation with existing measured data. However, aligning measurable model pools with long-term data sets has proven to be challenging. At this stage, the optimized parameters of SATURN have yet to be tested against an independent data set. In an effort to model the measurable we proposed a fractionation scheme that does not align with available data. Archived soil samples could prove to be a valuable resource for generating data sets for use in further tests of this, and other functional pool models. Other models have taken a more reductionist approach and designed model pools that represent the primary and basic components of SOC (Sohi 2001). The question was whether to ‘model the measurable’ or ‘measure the modelable’. We propose that the answer is somewhere in-between.

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