

DISSERTATION

MODELING SOIL ORGANIC MATTER: THEORY, DEVELOPMENT, AND APPLICATIONS IN BIOENERGY

CROPPING SYSTEMS

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ABSTRACT

MODELING SOIL ORGANIC MATTER: THEORY, DEVELOPMENT, AND APPLICATIONS IN BIOENERGY CROPPING SYSTEMS

Soil organic matter (SOM) is a complex, dynamic, and highly variable soil constituent that is of fundamental importance to many soil functions, terrestrial ecosystem processes, and biogeochemical cycles. Its importance extends across scales, ranging from site-specific impacts on soil fertility to the global net exchange of carbon between terrestrial systems and the atmosphere. Soil organic matter is impacted by human activities, as seen most directly in agricultural systems. In this context, SOM models play an important role in integrating the understanding of complex, interacting soil processes across temporal and spatial scales, contributing to land use decision making by providing comparative evaluation of soil impacts associated with different management practices. Crop-based bioenergy feedstock production systems are an emerging area for these types of SOM model applications. However, model evaluations are dependent on the theoretical basis of a given SOM model, as well as the quality of data used to drive the model for a given system or management scenario. This study therefore explores linkages between advances in the theoretical understanding of SOM dynamics, the development of SOM models to reflect these advances, and the application of SOM models to assess crop-based bioenergy production systems.

First, five emerging areas in SOM research were reviewed in the context of SOM models, including SOM stabilization mechanisms, saturation kinetics, temperature sensitivity, dynamics in deep soils, and incorporation into earth system models. These reviews demonstrated the importance of identifying where SOM model development and applications are most limited, whether in theoretical understanding, in model implementation, or in data availability. For example, SOM saturation kinetics is

theoretically well understood but remains difficult to implement in SOM models, only yielding improvements in a narrow set of ecological conditions. SOM temperature sensitivity and deep soil dynamics, however, are more limited by poor data availability in addition to poor theoretical understanding of interacting processes.

A selection of shortfalls in SOM modeling were then addressed and explored with the Litter Decomposition and Leaching (LIDEL) model, a litter decomposition model that incorporates dynamic microbial carbon use efficiency (CUE) and yields dissolved organic carbon (DOC) as one of the byproducts of litter decomposition. In this analysis a hierarchical Bayesian statistical approach was used to test model performance and estimate unknown model parameters using experimental data. While this analysis showed the LIDEL model successfully integrates hypotheses for litter nitrogen and lignin controls on dynamic microbial CUE and the generation of DOC from litter decomposition, there remains a great deal of uncertainty in the rate of microbial biomass turnover as well as the proportioning of biomass from microbial turnover between solid versus soluble microbial products. Targeted experimental evaluation of the generation of DOC from microbes versus litter would support greater certainty in these model parameters and further model development for more general applications.

Finally, the performance of the DAYCENT ecosystem model was evaluated in simulating US corn residue removal and Brazilian sugarcane production, two types of crop-based bioenergy feedstocks. DAYCENT is a process-based ecosystem model that integrates a soil organic carbon model to simulate carbon and nitrogen cycling processes through plant-soil interactions. The results of DAYCENT corn residue removal simulations highlighted several DAYCENT model biases, such as low corn yield estimates in dry regions and an overestimation of soil carbon loss with conventional tillage. Despite these biases, the results showed the importance of considering interactive effects between corn residue removal and other crop management practices in this type of bioenergy feedstock production system. The results suggest corn residue removal is ideally paired with management practices—such as reduced tillage—to

maintain or improve soil carbon stocks. The analysis of Brazilian sugarcane management practices also highlighted management practices poorly simulated by DAYCENT, in particular identifying the need to improve DAYCENT simulations of high N₂O emission conditions observed in mechanically-harvested sugarcane, perhaps by adding simulation of DOC movement across the soil profile. However, this analysis also identified a need for more accurate and consistent daily precipitation data to drive DAYCENT simulations of N₂O emissions from Brazilian sugarcane management practices, particularly as there is interest in regionally-scaled analyses of direct greenhouse gas emissions from sugarcane production in Brazil.

Taken together, the results of this study show the importance of a close connection between emerging areas in SOM theory, SOM model developments, and SOM model applications in crop-based bioenergy feedstock production systems. This connection allows for the identification of specific areas in need of further research, whether developing new modeling approaches or gathering additional data to parameterize, drive, and evaluate model simulations. This connection should remain a central emphasis as SOM models are increasingly incorporated into crop-based bioenergy policy and land management decision making.

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1 INTRODUCTION

Soil organic matter (SOM) is highly complex, often mysterious, and offers endless challenges to the understanding of its underlying dynamics. Soil organic matter also plays a fundamental role in natural processes across scales. These scales range from soil microsites where water, organic matter, nutrients, and oxygen, and living organisms interact to determine the fate of litter inputs (Davidson et al., 2014), to globally-scaled processes such as carbon (C) cycling between terrestrial systems and the atmosphere (Heimann and Reichstein, 2008). Soil organic matter is therefore an important consideration in land management, both in sustaining its value as a resource—e.g. supporting productive soils used for agricultural production—and in mitigating direct and indirect ecosystem impacts of human activities—e.g. the potential for loss of soil C due to land use conversion from native ecosystems into agricultural production (Searchinger et al., 2008). The understanding of SOM dynamics is therefore often linked to efforts to soil and ecosystem management, whether to improve soil health and productivity or to preserve key functions such as C storage.

In this context, SOM models play a key role in integrating understanding of complex, interacting soil processes across scales. Soil organic matter model development has continually advanced, with recent emphasis on testing hypotheses for the impacts of climate change on SOM dynamics and ecosystem processes. The climate impact assessment of crop-based bioenergy production systems is an example of an area where SOM models are seeing increasing application, in the context of greenhouse gas emission management and the development of sustainable land management practices. In these applications, SOM models provide a tool to project across temporal and spatial areas, contributing to decision making by providing comparative evaluation of GHG impacts associated with crop management practices. However the validity of these model evaluations are only as good as their basis in the scientific understanding of SOM dynamics.

The first part of this work, presented in chapter two, provides an extensive review of SOM modeling, discussing past developments, history, and giving an overview of the ‘toolbox’ common model formulations. Chapter two also provides a series of five short reviews on rapidly advancing areas in SOM modeling. These short reviews are on the topics of 1) recent ideas in SOM stabilization mechanisms, 2) saturation kinetics, 3) temperature controls on decomposition, 4) deep SOM dynamics, and finally concludes with 5) a discussion of SOM representation in earth system models.

Looking to address some of the shortfalls in SOM modeling discussed in chapter two, chapter three presents the Litter Decomposition and Leaching (LIDEL) model, a new modeling approach to litter decomposition that incorporates dynamic microbial carbon use efficiency and yields dissolved organic carbon (DOC) as one of the byproducts of litter decomposition. Other SOM models have been criticized for poorly accommodating either of these important components of litter decomposition. The LIDEL model provides a first step to a new approach to litter decomposition that would strongly advance simulation of DOC dynamics through the soil profile, recognized as an important component of deep soil C processes (Rumpel and Kögel-Knabner, 2010). Chapter three additionally presents a hierarchical Bayesian analysis for data-model integration, using this approach to estimate unknown LIDEL model parameters and compare the performance of four different LIDEL model formulations. This analytical approach accommodates the high variability and uncertainty in both measured data and model formulation that are commonly characteristic in SOM research.

The final two chapters then step out to a larger scale to explore the use of the DAYCENT model—a full ecosystem model that integrates the CENTURY soil organic carbon model to simulate C and N cycling processes in plant-soil interactions (Parton, 1987)—in simulating two types of crop-based bioenergy feedstocks. Chapter four provides a validation analysis of DAYCENT performance in simulating corn stover harvest for cellulosic ethanol in the United States. Chapter five then presents a

parameterization and validation analysis of DAYCENT model performance in South Central Brazilian sugarcane production systems.

Taken together, these four chapters contribute towards a more integrated connection between emerging areas in SOM theory, SOM model developments, and SOM model applications in crop-based bioenergy feedstock production systems. This connection is an important area of consideration as SOM models are increasingly incorporated into crop-based bioenergy policy and land management decision making. This study aims to demonstrate how connecting across SOM theory, SOM model development, and SOM model applications can allow for better identification of specific areas in need of further research, whether developing new modeling approaches or gathering additional data to parameterize, drive, and evaluate model simulations.

2 SOIL ORGANIC MATTER MODELING- PAST APPROACHES AND NEW CHALLENGES¹

2.1 Introduction

Many discussions of soil organic matter (SOM) research begin with a statement to the effect that soils are complex, challenging to study, and do not easily part with their mysteries. A new favorite term is ‘the Gemish effect’ (Davidson et al., 2014), referring to the challenge of identifying fundamental drivers in the hodgepodge of soil minerals, organisms, and organic matter cycling dynamically through space and time in the belowground environment. Apart from being recognized as the “most complicated biomaterial on the planet” (Young & Crawford, 2004, pg 1634), SOM is also a key component of ecosystem processes and biogeochemical cycles, notably including the responses to and sustainability of human impacts on the earth. The study of SOM further requires wrestling with the logistical challenges of soil opacity and observer effects—where what is observed is changed by the process of observation—as well as the conceptual challenges of integrating interactions between multiple factors across scales. It is with the latter that simulation models for SOM dynamics play a crucial role in SOM research.

In soil science and ecology, simulation models serve many purposes ranging from mathematical formalization of hypotheses to projecting processes across space and time. Models are meant to provide a useful simplification of reality. Yet even after over a century of study there are few hard rules in the understanding SOM dynamics. Some of this is driven by the logistical challenges of measuring soils. Soils are difficult to characterize in ways that account for their complexity and heterogeneity across systems, scales, and depths. SOM model testing is therefore routinely data-poor, particularly across large scales and long periods of time. However other uncertainties arise from using measurements of operationally defined (e.g., by mesh size, chemical extraction, density) soil fractions to evaluate and compare SOM

¹ In preparation with K. Paustian for a chapter titled “Simulation Modeling” in *Methods of Soil Analysis: Soil Organic Matter*, edited by R.F. Turco.

dynamics. Soil fractionation methods are recognized to have variable linkages to mechanisms that affect SOM and drive its ecological behavior (von Lützow et al., 2007; Wander, 2004). Bulk soil dynamics are not easily reconstructed from measurement of its parts.

Simulation models of SOM therefore play a key role in SOM research and application by supporting hypothesis testing and predictions that are often infeasible by direct measurements, and more importantly, by providing an explicit mathematical framework for considering the structure and dynamics of SOM. The linkage between SOM measurements and conceptual understanding of SOM dynamics is accordingly at the foundation of SOM model structure. For example, some SOM models are formulated with conceptual, kinetically-defined SOM pools, that are not directly measurable *per se*, but have been proven through decades of testing as general models that work reasonably well to simulate bulk soil dynamics, particularly over the long-term (e.g., Jenkinson & Rayner, 1977; Parton et al., 1987). Other emerging SOM models take different approaches to SOM dynamics—e.g. defining SOM pools by specific SOM mechanisms or as analytically measurable SOM fractions. However, many of these models currently remain more limited in their applications, either due to simplification of factors that are important at larger scales, or due to limited data availability (Davidson et al., 2014; Segoli et al., 2013; Tipping et al., 2012). Ideally, a SOM model would be based on mechanistic understanding of SOM dynamics, use SOM pools that can be informed by measured data, and apply across multiple scales. At this point in time, however, no single SOM model yet fits this ideal and indeed inherent tradeoffs between model attributes (e.g., generality, predictive capacity, complexity) relative to their intended purpose suggest that no such ideal model **can** exist (Levins, 1966; Sharpe, 1990).

Jenny's now classic factors of soil formation, informed by even earlier work (Hilgard, 1906; Dokuchaev, 1883), provides a useful framework to examine the complexities SOM dynamics, presenting the interaction of soil forming factors as;

$$S = f(cl, o, r, p, t, \dots) \qquad \text{Eqn 1}$$

such that a particular soil attribute (S) is a function of climate (cl), organisms (o), topography (r), parent material (p), time (t) and other factors that often include human activities (Bidwell and Hole, 1965; Jenny, 1941). This approach has formed the conceptual underpinning of many process-based soil and ecosystem models (Vitousek, 1994). We argue that it continues to act as an overarching framework in SOM modeling, providing a common thread to evaluate how current hypotheses for SOM dynamics are reflected in SOM models applied across scales.

Development of SOM models moves hand-in-hand with conceptual understanding of SOM dynamics and their linkages to SOM measurements. In recent years, new hypotheses for SOM persistence have led to reformulation of SOM models to explore explicit simulation of microbial biomass and more mechanistically-based microbial decomposition mechanisms. Researchers have also examined the mechanism of SOM saturation as a limitation on soil carbon storage. Expanding efforts to aggregate SOM data and complete large-scale multi-model testing are also pushing SOM model development forward. These efforts have been driven in part by the potential role of SOM as a sink or source of atmospheric CO_2 , with implications for global climate change. Temperature sensitivity of SOM decomposition with warming climates has consequently been brought under greater scrutiny, alongside increased interest in simulation of SOM dynamics in deep soil layers. Global and earth system models, which are now incorporating SOM models of increasing complexity, are an area for soil scientists to both evaluate SOM hypotheses at a global scale, as well as support better model development and accuracy through model-data integration.

In this review we first provide some background and history of SOM model development, as well as brief summaries of modeling approaches and their linkages to SOM measurements and the conceptual understanding of SOM dynamics (Section 2.2). We will then review a selection of recent advances in SOM modeling that we believe are particularly relevant to ongoing SOM research. These include: new ideas in SOM stabilization, modeling SOM saturation kinetics, temperature controls on

decomposition, SOM dynamics in deep soil layers, and finally a review of SOM representation in earth system models (ESMs) (Section 2.3).

2.2 SOM modeling, past and present

2.2.1 Basic modeling concepts and terminology

There are several general differences in approaches to mathematical modeling. The first is the difference between an **empirical** versus a **mechanistic** model. An empirical model is data-driven, making predictions based on observations of a relationship or interaction, without explicitly defining the underlying causal mechanisms. A mechanistic model, on the other hand, is based on a representation of mechanisms that drive dynamics in a system, using a ‘first principles’ approach (i.e. starting with the most basic assumptions) to build a predictive model. The latter is often a more defensible foundation for an explanatory model, but is hard to come by in ecology and biogeochemistry where system dynamics typically result from complex, heterogeneous, interactive factors that are often not fully understood.

Whether empirically- or mechanistically-based, models can be **static** or **dynamic**, the former referring to a model of a system at a fixed point or interval of time while the latter explicitly includes changes through time. Models can also be either **stochastic** or **deterministic**. Stochastic models include random variation in model simulations, while deterministic models do not. In a deterministic model the same initial conditions and model parameters will always generate the same result, while stochastic model results will have some degree of random variability. Many processes in ecology and biogeochemistry are variable and change through time. Stochastic and dynamic models are often a closer representation of these types of systems. However, stochastic and dynamic models are also typically more complex and computationally intensive, which may limit their use. Models are ideally as simple as possible, while still serving as an effective representation of reality.

As commonly used terminology, a model **pool** refers to a quantity of material. For the purposes of this review model pools are generally quantities of OM or C. A **flux** is the rate at which material

moves from one pool to another or into a larger **sink** or **source** external to the system being simulated.

A **parameter** controls the dynamics of the system and can either be a constant or variable, depending on whether it is a set value or informed by other internal (e.g. pools or fluxes) or external (e.g. driving variables) components of the system. Figure 2-1 gives a visual representation of a set of dynamic, deterministic models with structures commonly used in SOM models, representing pools as boxes and fluxes as arrows.

2.2.2 History overview of SOM modeling

The origins of mathematical modeling of SOM processes, we would argue, largely stem from two main areas of inquiry. First, several early models were developed to describe the rate of mass loss of plant residues and the relationship between plant residue inputs and soil organic matter levels (Hénin and Depuis, 1945; Jenny et al., 1949; Salter and Green, 1933), including the observed loss of SOM following conversion of native ecosystems to cropland (Jenny, 1941). These were formulated as single pool models with first-order decay kinetics for mass loss, vis,

$$\frac{dC}{dt} = I - kC \quad \text{Eqn 2}$$

at equilibrium(C^*), $\frac{dC}{dt} = 0$, then,

$$C^* = \frac{I}{k}, \quad \text{Eqn 3}$$

where C is SOC (or plant litter C), I is organic C input and k is the specific rate of decay. This simple formulation expresses the fundamental concept that (in a stable environment) SOM content (or plant litter stock) tends towards an equilibrium state given by the balance between plant carbon litter inputs (I) and SOM C decay, which can be defined by an overall mean residence time (equal to $\frac{1}{k}$) of C in soil (Olson, 1963).

A second area of early mathematical modeling concerned the dynamics of nitrogen, given its many recognized states in soil and particularly with the advent of ^{15}N as a tracer, models were

formulated to describe and interpret the results of isotopic mixing and N transformations between different forms in soils (Jansson, 1958; Kirkham and Bartholomew, 1954). For early models of both soil C and N dynamics, models needed to be solvable using analytical methods and thus representation of SOM was highly simplified, usually as a single 'homogeneous' pool. Although the heterogeneity of SOM, in the sense that it is comprised of many different forms of organic matter decomposing at different rates, was clearly recognized (e.g. Waksman, 1926; Waksman & Stevens, 1930), this key aspect of SOM was not addressed in early models, likely due to the practical mathematical reasons stated above.

With the widespread availability of digital computers and programming languages beginning in the late 1960s, along with the establishment of the International Biological Programme (IBP) and its goal of computer modeling of whole ecosystem dynamics (Innis, 1978), more complex models, which included soil organic matter dynamics formulated with multiple SOM pools, continuous driving variables (e.g., temperature, moisture) and a more mechanistic treatment of controls on decomposition and stabilization factors, were developed (e.g., Hunt, 1977; Smith, 1979; McGill *et al.*, 1981). Arguably, one of the motivations affecting the formulation of this first generation of computerized models was a desire for comprehensiveness and detail in the components and processes known to be of importance. Hence, in several models, explicitly including microbial biomass components as explicit state variables controlling decomposition and transformation of non-living litter and SOM pools was axiomatic. While useful as explanatory and research models, the strong feedbacks between microbial biomass and organic matter pools and high sensitivity of the models to poorly-understood parameters controlling microbial growth and mortality, yielded model stability problems and made the models less suitable for predictive purposes. Subsequently, the vast majority of ecosystem-scale models of SOM dynamics developed during the 1980s and 90s (e.g. Smith *et al.*, 1997) retained a multiple-pool approach and a relatively comprehensive inclusion of dynamic environmental drivers, but reverted back to a first-order kinetics paradigm. In these models the role of microbes and other decomposer organisms are certainly

implicit, and their responses are represented by rate modifying functions determined by dynamic environmental and management conditions, but the actual quantity or biomass of decomposer organisms are not included as a rate control. This mainstream approach largely continues to this day, although as discussed in the third section of this review, there is an ongoing reexamination of this dominant paradigm and an exploration of ways to more explicitly represent microbial controls on SOM transformations.

2.2.3 SOM modeling approaches

The 'toolbox' of mathematical approaches to SOM modeling has seen relatively little recent change or expansion (Parton et al., 2015). Rather, advancements in SOM modeling are largely derived from new linkages between mathematical approaches and conceptual understanding of SOM dynamics. In this section we present a basic summary of mathematical modeling and applications to SOM, as background to more recent developments in SOM models reviewed in Section 2.3.

2.2.3.1 First order kinetics – dominant multi-compartment models

1st order decomposition kinetics are a modeling approach where the flux of material from a pool is linearly related to the quantity of material in that pool (Figure 2-1, A & B). 1st order kinetics are a mathematically simple expression of decomposition that continues to dominate SOM modeling. It is also a mathematical approach that lends itself more easily to analysis of steady-state conditions, particularly when applied to a single pool model where the steady state is proportional to the input divided by the decomposition rate (Eqn's 2 & 3, detailed derivation in Stewart *et al.*, 2007).

As described above, a single-pool SOM model using 1st order kinetics is one of the simplest mathematical approaches to simulate a dynamic relationship between SOM and decomposition processes (Figure 2-1, A). A single-pool approach has been used to simulate SOM dynamics (e.g. Giardina & Ryan, 2000). However, the most common SOM model structure uses multiple pools to simulate SOM dynamics, each pool acting under 1st order kinetics but with different rates of change and

input movement from one compartment to another (Figure 2-1, B) (Paustian, 1994). The widely-used CENTURY model reflects this approach, using three compartments that reflect pools containing fast, slow, and passive SOM as well as additional pools representing fresh plant residues (Parton et al., 1987). As will be discussed in Section 2.3.5, this type of structure is particularly common within models applied at high spatial scales (e.g. Earth System Models (ESMs)), by serving as a relatively simple mathematical approach that dynamically represents decomposition across heterogeneous SOM. However, it is increasingly critiqued as having limited ability to reflect new understanding of mechanisms driving SOM dynamics (Todd-Brown et al., 2012).

2.2.3.2 Organism-oriented and non-1st order kinetic

There are currently two main areas of development in SOM models exploring alternative approaches to 1st order kinetics. The first centers on an old debate described above, specifically: how are soil organisms represented in SOM models? Decomposition processes are obviously dependent on microorganisms. However, 1st order decomposition models like CENTURY implicitly model microbes through controls on decomposition rates while lumping microbial biomass within kinetically-defined SOM pools. This approach is based on the assumption that the soil microbial community can respond quickly to changes, and their biomass will therefore not limit the rate at which decomposition processes occur (Paustian, 1994). Early models like PHOENIX took a more organism-oriented approach, explicitly simulated microbial biomass as a direct control on decomposition rates (McGill et al., 1981). These types of models were more commonly applied to examine soil food webs and energy flow through the soil environment (Paustian, 1994). However, 1st order kinetic models represented a simpler approach shown to perform well simulating a wider array of SOM responses, and therefore gained more widespread acceptance and use than organism-oriented models for ecosystem-scale soil C dynamics (Stockmann et al., 2013).

Recent ideas in SOM persistence have brought explicit microbial models back into focus, where microbial biomass is included as a SOM pool that affects SOM decay rates (Figure 2-1, C). It is not yet clear if returning to these approaches yields improvements in model simulations across scales, but there are rapidly developing efforts exploring these mathematical approaches. This will be discussed in more detail in Section 2.3.1.

A perhaps less contentious topic is the implementation of saturation kinetics within SOM models, where the quantity of material in a pool—relative to a maximum amount—affects the flow of material into that pool (Figure 2-1, D). This is a reasonably straightforward, defensible SOM concept. However it adds mathematical complexity to SOM models relative to 1st order kinetics. It is also not yet certain how to quantify saturation capacity for a given SOM pool. Despite repeated observation of saturation kinetics, this is a dynamic that has had little successful implementation in SOM models. Saturation kinetics in SOM modeling will be discussed in more detail in Section 2.3.2.

2.2.3.3 Conceptual vs. measurable SOM pools

Linking measurable SOM fractions to modeled SOM pools has been long recognized as an important area of development in SOM modeling (Elliott et al., 1996; Paustian, 1994; Stockmann et al., 2013). In the absence of this linkage, the dynamics of individual SOM pools cannot be directly compared against measured pool quantities to evaluate their accuracy in SOM simulations. This creates a strong potential for equifinality, where the same results can occur through different means (Luo et al., 2012; Tang and Zhuang, 2008), often referred to by the more colloquial phrase of ‘getting the right answer for the wrong reasons’.

An additional benefit of linking SOM measured fractions to modeled SOM pools would be to reduce the uncertainty inherent in ‘spin-up’ equilibrium simulations needed to initialize conceptual (non-measured) SOM pools. The spinup method of SOM model initialization is based on the assumption that the underlying SOM pools are distributed with reasonable accuracy if the equilibrium simulations

match the initial conditions of the experiment being simulated, and therefore model pools 'self-initialize' as a function of their mathematically-defined turnover rates. This is the best method available to use a multi-pool model when, as in the case of most SOM models, the initial conditions of the pools are not measurable. Spin-up simulations often need to be run for tens, hundreds, or even thousands of simulated years, and therefore drastically increases the time required to complete experimental model simulations. In the case of large-scale analyses this can place a logistical limit on simulation complexity and applications (Xia et al., 2012). Direct measurements of SOM pools would remove the need for spin up simulations entirely, by making starting conditions equal to those known to exist in soils directly. On the other hand, determining initial pool sizes based on direct-measurement of the modeled pools would necessarily require that the soil measurements are in fact made, which could be a major constraint for large-scale regional and global model applications.

However, the fact that this topic continues to be recognized as a challenge in SOM modeling is expressive of the remaining uncertainty linking measurement of SOM fractions to conceptual understanding of SOM dynamics. Benchmarking data have been suggested to reduce equifinality (Luo et al., 2012). Increases in computational capacity has also allowed for innovations in data assimilation and the increasing use of Bayesian statistical approaches to constrain model parameters (Braakhekke et al., 2013; Luo et al., 2011). Until a SOM measurement method yields consistently SOM fractions uniform in their kinetic or biochemical behavior, the linkages between SOM measurements and modeled SOM pools will remain unclear (Dungait et al., 2012; Wander, 2004). Linking modeled SOM pools to measurable soil fractions remains an important area in the development of SOM model-data integration. In the meantime the type of measurements being analyzed as well as the scope and scale of the question being asked needs to guide model selection, as some models are more suited to certain types of analyses than others (Manzoni et al., 2012).

2.2.3.4 Data-model integration in SOM research

A detailed discussion linking specific measurement methods to pools and dynamics within SOM models is beyond the scope of this work, with the exception of examples in topics reviewed in Section 2.3. However, we suggest exploring previous research examining this linkage between SOM measurements, conceptual understanding of SOM dynamics, and SOM models in greater detail (Dungait et al., 2012; Simpson and Simpson, 2012; von Lützow et al., 2007; Wander, 2004). Here we will instead step back and make a few points about the integration between data and models in SOM research and SOM model development.

First, there are several ways SOM models and SOM data interact. These can be grouped into three general categories: using data to *formulate* a SOM model, using data to *drive* a SOM model, or using data to *evaluate* a SOM model. Data used to *formulate* SOM models are tied to the hypotheses that a model represents. An example: using incubation data from warming experiments to mathematically define a SOM decomposition temperature response curve (e.g. Parton et al., 1987). Empirical, data-driven relationships are used in models when factors are known or hypothesized to impact SOM processes, but underlying mechanisms are either unknown or not fully understood. Data can also be used to parameterize components of an SOM model, optimizing model performance by ‘tuning’ parameter values to data when parameters are not measured directly. Data to *drive* a SOM model, on the other hand, are typically based on external factors known or hypothesized to force SOM behavior. These data, depending on their scale and variation, can link spatial and temporal heterogeneity to simulated SOM dynamics. These data often tie back to Jenny’s factors of soil formation (Eqn 1), for example with air temperature and precipitation (climate), soil texture (parent material), and vegetation (organisms) commonly used in simulating SOM dynamics in ecosystem, global, or earth system models. Finally, data to *evaluate* SOM models are fairly self-explanatory, used to validate model

performance, evaluate uncertainty, and finally support hypothesis testing through the comparison of SOM simulations with measured results.

These categories help clarify some of the pitfalls in model-data integration. From the *formulation* side, data link to the hypotheses mathematically represented by a model. New data may therefore prompt model changes, for example if new data alter the shape of an empirical relationship built into model structure, or if new measurement methods yield entirely new hypotheses for SOM processes. In any case, data used in model *formulation* require careful consideration to ensure a model accurately represents hypotheses for SOM dynamics. The information to *drive* SOM models tends to be more sensitive to data limitations, particularly across scales. Data limitations for *drivers* affect how spatial and temporal heterogeneity are represented in the simulation of SOM dynamics, potentially leading to biased or erroneous results. Model *evaluation* experiences similar limitations determined by the scale at which an SOM model is being applied. Data availability for model *evaluation* will affect assessment of model accuracy, uncertainty, as well as its ability to support hypothesis testing.

The full suite of data for model formulation, driving, and evaluation are not always easy to identify or compare between SOM models, particularly when they are integrated into large-scale ecosystem or global models. Measurement uncertainty is also a consideration across all three types of data-model integration. Neither challenge is new (Keenan et al., 2011). However, in recent years researchers have targeted these challenges using rapidly advancing computational capacity, developing networks that bridge between SOM data and models. These efforts are aimed to support an iterative cycle of data-model integration. Components of this cycle includes data standardization, increasing data acquisition and accessibility to models, identifying and targeting data-poor areas of research (e.g. tropical soils), model benchmarking, and ideally multi-model comparisons (e.g. Luo *et al.*, 2012). These efforts provide a better environment for model development, and hypothesis testing. Large scale data-model integration is increasingly recognized as a multidisciplinary effort with high value for SOM

research. This is an area of development that will likely continue to advance, potentially dramatically and in the near future.

2.3 New directions in SOM model development

We now present a series of short reviews on selected areas in SOM research of particular relevance for the use and development of SOM models. We emphasize areas where SOM modeling and experimental research can greatly benefit by integration and collaboration. A recurring theme is the challenge of integrating understanding across scales.

2.3.1 Recent ideas for SOM stabilization mechanisms

Researchers have studied SOM dynamics for over a century, understanding with increasing sophistication how the quantity, quality, and cycling of SOM play important roles in soil functions (e.g. hydrology and water holding capacity), soil fertility (e.g. nutrient availability and cycling), and ecosystem processes (e.g. net exchange of carbon and energy flow) (Manlay et al., 2007; Wander, 2004). However, a fundamental area for SOM research, including SOM modeling, are the linkages between SOM cycling processes and SOM persistence. In other words: what controls the persistence of macromolecules in the soil against the pervasive presence and activity of organic matter mineralizing microorganisms and microbial enzymes?

For decades, stabilization mechanisms and SOM persistence have been integral components of research on SOM cycling and the development of SOM models (Campbell *et al.*, 1967; Jenkinson & Rayner, 1977; Parton et al., 1987; Oades, 1988). It continues to be a predominant research topic (Dungait et al., 2012; Kleber, 2010; Schmidt et al., 2011), of particular importance to understand the role of soils in the global C cycle and to determine their potential to either contribute or mitigate atmospheric greenhouse gas (GHG) emissions (Friedlingstein et al., 2001; Jobbagy and Jackson, 2000; Schimel, 1995). Soil organic matter turnover and stabilization mechanisms have been subject to numerous recent reviews (Table 2-1) and we will not tackle an exhaustive update to these previous

works. Rather we will focus this section on a major shift in one of the dominant conceptual paradigms for SOM stabilization, equating SOM chemical complexity with resistance to enzymatic attack and thus its longevity in soils. New observations of SOM chemical characteristics and behavior have provided evidence against inherent SOM chemical complexity as a dominant mechanism for long-term SOM stabilization (Dungait et al., 2012; Kleber et al., 2011; Schmidt et al., 2011; von Lutzow, 2008). New hypotheses have led to re-evaluating SOM modeling approaches as well as increasing exploration of more organism-oriented models explicitly linking microbial biomass and microbial mechanisms to SOM dynamics.

Stepping back, we would first like to link SOM persistence more generally to our previous discussion connecting SOM fractionation methods, modeled SOM pools, and conceptual understanding of SOM dynamics. Organic matter is a high-energy organization of molecules created and maintained by living processes that—upon death and particularly in the presence of the ubiquity of microbes and microbial enzymes—should decompose, forming new bonds at lower energy states (Hedges et al., 2000; Kleber, 2010; Schmidt et al., 2011). The persistence of OM in soils indicates widespread operation of protective mechanisms that slow or prevent OM decomposition from occurring in the soil environment.

Linking protective mechanisms to SOM persistence is, however, challenged by their temporal variability and tendency to interact. For example, some OM inputs are accessed quickly by soil microbes, mineralized within minutes, hours, or days. However, OM that becomes protected from microbial activity, e.g. tightly bound to soil minerals within micro-aggregates or more temporarily stabilized by roots or fungal hyphae within macro-aggregates (Golchin et al., 1994; Oades, 1984; Pronk et al., 2012; Six et al., 2004; Six and Paustian, 2014; Tisdall and Oades, 1982), can remain in soils for years, decades, centuries or even millennia depending on factors driving the dynamics of protective mechanisms (e.g. Oades, 1988; Jastrow, 1996). The net result of interacting stabilization mechanisms are soils containing

SOM that is a mixture of ages at different stages of decomposition, and that potentially react differently to change (e.g. land use or climate) (Paul et al., 1997; Schimel et al., 1994; Trumbore, 2000).

Experimentally isolating the mechanism or interaction of mechanisms that determine SOM persistence also remains difficult, as some mechanisms operate over extended time periods, and experimentally studying mechanisms often requires changing some of the conditions that affect them. Laboratory soil incubation studies, for example, must account for changes in soil structure and the effects of isolation from the *in situ* plant-soil system. Due to logistics and the development of increasingly unrealistic conditions in laboratory incubations through time, there is also predominance of short-term laboratory experiments evaluating more rapid SOM cycling mechanisms (Conant et al., 2011). Long-term field experiments begin to account for slower soil mechanisms and interaction between multiple factors *in situ* (Paustian et al., 1995), but these experiments can only cover so much ground and are still relatively 'short-term' for some soils processes, even with the longest (at Rothamsted, UK) having recently surpassed 170 years (Jenkinson and Rayner, 1977). Isotopic analyses using ^{14}C 'bomb carbon' labeling from atmospheric nuclear testing has high value for estimating responses of slow SOM mechanisms (Trumbore, 2009, 2000). It is also possible to evaluate longer-term SOM dynamics using other isotopic C labels, or natural changes in ^{13}C abundance when vegetation shifts between a dominance of C3 and C4 plants (Kuzyakov and Domanski, 2000). A combination of approaches and the use of non-C tracers can also be revealing in a given soil environment (Braakhekke et al., 2013; Kuzyakov and Domanski, 2000).

Regardless of experimental approach, bulk SOM dynamics are generally not fully informative of underlying mechanisms and can even mask important short-term dynamics when, as is common, total SOM mass is dominated by older, more slowly cycling material (Trumbore, 2000). Therefore SOM stabilization, turnover rates and persistence are typically evaluated in association with SOM fractionation methods. The age of bulk SOM ranges on average from decades to centuries, associated

with kinetic dynamics across soil fractions that exhibit patterns most consistent at kinetic extremes, e.g. the slowest turnover rates of hundreds to thousands of years associated with tightly mineral-bound OM, while the fastest turnover rates of weeks to a few years associated with fresh litter inputs (Balesdent, 1987; Campbell et al., 1967; Scharpenseel and Becker-Heidmann, 2006; Trumbore, 2009; von Lützow et al., 2007). Unfortunately SOM cycling at either extreme tend to make up a relatively small quantity of SOM, with the remainder cycling somewhere in a decade-to-century continuum that is, as discussed above, difficult to separate into fractions with uniform kinetic or biochemical characteristics.

Simulation models for SOM dynamics therefore play a key role integrating understanding in a mathematical framework that allows for broader and more rapid hypothesis testing than feasible through direct experimentation and measurement alone (Schimel et al., 1994). Models such as CENTURY and RothC—both still widely used today—are based on multiple 1st order dynamic SOM pools assigned different kinetics, or rates of change through time (Jenkinson and Rayner, 1977; Parton, 1987). While the multi-pool 1st order kinetic approach has been shown to successfully represent the heterogeneity of SOM decomposition and improve model predictions (Carpenter, 1981; Trumbore, 2000), these pools remain conceptually defined. There have been efforts to link modeled SOM pools to specific measured SOM fractions (e.g. Zimmermann *et al.*, 2007), but this is difficult particularly for slowly cycling SOM pools where the linkages between measure pools, stabilization mechanisms, and decomposition rates remain unclear.

It is within this context that a new understanding of SOM chemical complexity and its role as a mechanism for SOM persistence can be more thoroughly explored. Until recently mechanisms for SOM stabilization were generally grouped into three categories: 1) physical protection from microbial processes (e.g. through aggregate formation), 2) mineral associations that limit exposure to lytic enzymes, and 3) increasing OM recalcitrance by selective preservation of less biodegradable litter inputs and the formation of complex, stable humic molecules (Six et al., 2002; Sollins et al., 1996; von Lutzow,

2008). Mineral associations and physical separation continue to be recognized as important SOM stabilization mechanisms. They can be explored in greater detail in the reviews listed above (Table 2- 1). However the hypothesis that a main mechanism for long-term SOM persistence is the gradual transformation of primary biomolecules into complex secondary ‘humic’ molecules resistant to decomposition has been largely refuted.

The origin of the hypothesis linking inherent chemical complexity to SOM stability—what has been termed ‘biochemical protection’ or simply ‘recalcitrance’ (Six et al., 2002; Sollins et al., 1996)—traces back to early research on soil humus. We refer to a historical accounting of SOM conceptual development by Manley et al. (2007) for greater detail, but here will summarize a few key points. Humus saw its first use as scientific term in the late 1700’s/early 1800s, referring to the dark material accumulating in soils with the decay of dead plants and animals. One of the earliest linkages of humus to SOM as a soil constituent was in Albrecht Thaër’s *Principles of rational agriculture* (1809). The connection between humus and soil fertility drove subsequent research to understand its development and behavior, particularly in the context of plant nutrition and soil nutrient availability (Manlay et al., 2007). This included exploring various measurement methods to separate humus into meaningful fractions, notably including acid and alkali extraction that yielded fractions with varying decomposition behaviors in soil incubation. It is worth noting that as early as 1938 an argument was made against the use of these chemical fractionation methods—at least to characterize humus—due to their dubious linkages to underlying soil processes:

“Practically all the methods suggested at various times for determining the amounts of “humus” or of the “humified” portions of the organic matter in soils, peats, and composts are unsuitable for this purpose, primarily because they were developed with little or no regard to the processes that take place when fresh organic matter undergoes decomposition...One is justified in speaking of humus only in regard to the sum total of the organic matter in soils, peats or composts. A study of the nature of this humus involves an investigation of the chemical nature of the plant and animal residues from which it originated, of the chemical processes of decomposition involved in its formation, of the nature and activities of the microorganisms bringing about the decomposition, as well as of the environmental conditions under which the decomposition took place.” (Waksman, 1938, pg 87-88)

Some of the above should sound familiar from our introduction and Section 2.2. Clearly the challenge of linking measured OM fractions to conceptual understanding of underlying processes has taxed many generations of soil scientists!

The emergence of ecosystem ecology and the increasing focus on SOM as a component of biogeochemical cycles saw a gradual shift away from the use of humus as a scientific term in these fields, as concepts behind humus formation and dynamics fit within the purview of SOM processes and dynamics. Humus and humification came to be viewed more as classic soil concepts, referring to microbially and chemically processed organic matter resistant to further decomposition and the process that creates it, respectively (Lützwow et al., 2006). However the chemical fractionation approach to characterize SOM by acid and alkali extraction, originating in humus theory and tied to the concept of isolating the large, complex organic molecules inherently resistant to decomposition (Schnitzer and Khan, 1972), largely remained, supported by radiocarbon dating that showed its isolation of SOM pools that cycled at different rates (Leavitt et al., 2006; Paul, 1984; Paul et al., 1997). This was generally referred to as the Humic Polymer Model (Brady and Weil, 2007).

Arguments against this theoretical approach and application of fractionation methods clearly are not new (e.g. Waksman, 1938). However, it is largely in the last decade that the weight of evidence against this hypothesis accumulated (Simpson et al., 2007; Stockmann et al., 2013), particularly based on new measurements for SOM chemical forms *in situ* as well as re-examination of the alkali- and acid-based chemical SOM fractionation method. Closer examination of the molecular nature of humic molecules have lent more support to the hypothesis that they have supramolecule structures—clusters of small molecules stabilized by hydrogen bonds and hydrophobic interactions, capable of forming micelles in aqueous solution and changing structure under different chemical conditions—rather than large polymer structures (Piccolo, 2002). Analyses also support that the behavior of humic molecules links more to the underlying properties that characterize molecular interactions, rather than the

chemical composition of humic molecules themselves (Sutton and Sposito, 2005). The link between acid and alkali extraction and SOM fractions with varying resistance to decomposition were shown to be largely a result of the extraction method, rather than indicative of underlying SOM chemical differences (Kelleher and Simpson, 2006). These extraction methods were further recognized to yield data with poor explanatory power for underlying SOM dynamics (Lützow et al., 2006; Wander, 2004). Within the soil *in situ*, evidence supported the characterization of SOM as a complex mixture of smaller biopolymers with complex spatial distribution in the soil matrix, rather than as large complex humic molecules (Lehmann et al., 2008). Ultimately, evidence supported decoupling inherent SOM chemical complexity from SOM persistence. As summarized by Kleber (2010); “recent investigations...revealed that significant quantities of organic material in soil may persist in spite of being chemically labile, unprotected, accessible, and decomposable” (pg 325). New hypotheses have emerged, centered on linking microbial processes with OM input chemistry and properties of the soil matrix (Cotrufo et al., 2013; Dungait et al., 2012; Gleixner, 2013; Schmidt et al., 2011). These hypotheses have invigorated an enduring debate in SOM modeling: to what degree should microbes and microbial mechanisms be explicitly represented in SOM simulations?

As mentioned in Section 2.2, the implicit versus explicit simulation of microbes and microbial processes in SOM models is a debate that dates back to the 1970’s, when explicit microbially-based models such as PHOENIX emerged alongside models, such as RothC and CENTURY (Jenkinson et al., 1987; Jenkinson and Rayner, 1977; McGill et al., 1981; Parton, 1987). The latter models performed more successfully simulating long-term SOM changes, based on the assumption that litter quality and environmental factors (i.e. temperature, moisture, and soil texture) are the main drivers of SOM turnover. However, while these types of models have been shown to predict long-term SOM dynamics well they perform more poorly over transient dynamics and short-term change, both of which are important in the context of predicting impacts from climate change (Lawrence et al., 2009). Interest in responses to climate change combined with rapidly advancing methods to study microbial processes

have resulted in a renewed interest to explicitly connect microbial mechanisms to models of SOM dynamics (Stockmann et al., 2013).

Hypotheses have been developed linking variable microbial growth efficiency (MGE) to decomposition processes (e.g. Moorhead & Sinsabaugh, 2006; Sinsabaugh *et al.*, 2013). Previously some of these concepts were explored in the Q- model, which explicitly included microbial growth rate and assimilation efficiency effects on SOM turnover (Bosatta and Ågren, 1991), tied to measures of litter chemistry to model C decomposition and SOM accumulation (Ågren and Bosatta, 1996). A recent synthesis of theory is provided by the Microbial Efficiency-Matrix Stabilization (MEMS) hypothesis, based on evidence that stable SOM is predominantly comprised of microbially-processed organic matter. The MEMS hypothesis suggests the potential for greater stabilization of more labile plant material, as high microbial growth efficiency would reduce OM lost to respiration during decomposition, increasing the creation of microbial products that could then persist by interactions with the soil matrix (Cotrufo et al., 2013). There have been some successes with representing variable MGE within SOM models in large-scale analyses (Wieder et al., 2013).

Other modeling approaches are exploring the connection between microbial community structure and SOM stabilization. This might be implemented by modeling the presence or absence of 'narrow' microbial community functions, such as N fixation or lignin degradation that are only accomplished by certain types of enzymes created by a small subset of microbes (McGuire and Treseder, 2010). The guild-based decomposition model (GDM) provides one such model of this type, with a structure based on microbial affinity for different types of substrates, as regulated by changing litter lignin and N characteristics over the course of decomposition (Moorhead and Sinsabaugh, 2006). The Microbial-Mineral Carbon Stabilization (MIMICS) is another example, linking microbial community functional groups (specifically, r- versus K- strategists), litter chemistry, and SOM stabilization through dynamic microbial growth efficiency. They hypothesize that the greatest SOM stabilization in sandy soils

occurs with low quality litter inputs due to biochemical protection versus the greatest SOM stabilization in fine-textured soils with high quality litters due to physical protection of microbial products (W. R. Wieder et al., 2014). In both cases, these models are largely theoretical and difficult to test in complex soil environments, as measurements of microbial community functional groups are not well established. Measurement methods, such as the use of genetic markers to quantify soil microbial community functions, is an area of active development that will allow for these types of hypotheses to be tested more explicitly.

The role of mycorrhizal fungi in SOM stabilization is another area of recent interest. Researchers have shown that plants in symbiotic relationships with mycorrhizal fungi can compete directly with free-living microbes for nitrogen (N) (Chapman et al., 2006). Mycorrhizal fungi, in particular ectomycorrhizae and ericoid mycorrhizae (EEM), secrete enzymes that allow them—and their plant symbiotes—to access organic N directly. However not all mycorrhizal fungal associations are equal in this regard, with arbuscular mycorrhizae providing more limited access to organic N. These differences led to the hypothesis that plants with different types of symbiotes would compete differently with free-living microbes for N, leading to varying degrees of microbial decomposition repression with concordant impacts on total SOM (i.e. better mycorrhizal-based competition for resources = more repression of free-living microbes = more SOM). This hypothesis was evaluated and supported at a global scale, across climate, clay content, and biomes (Averill et al., 2014). Additionally, a study of SOM accumulation in boreal forests due to root-fungal interactions demonstrated long-term continual SOM accumulation in the absence of disturbance. This suggested an alternative to SOM stabilization from aboveground litter inputs whereby SOM layers “grow from below” (Clemmensen *et al.*, 2013, pg 1617). Cumulatively these results suggest mycorrhizal fungal associations are an important consideration in SOM stabilization across scales, and may be a fruitful avenue to consider in refining SOM models.

In the midst of these developing areas of research, it remains difficult to determine whether microbial mechanisms improve SOM predictions, largely due to lack of data to either drive or validate new models (see Section 2.3.5). For example, a review of conventional versus microbially-based model performance was largely inconclusive, since microbial models with promise were limited by lack of data from larger scale application and benchmarking (Treseder et al., 2012). This will not always be the case, as ongoing studies target filling in these data gaps. In terms of SOM stabilization, the new understanding of SOM chemical characteristics and interactions with microbial processes have created many new testable hypotheses that will continue to develop as data are accumulated (Rillig et al., 2007). We suggest an emphasis on testing new hypotheses across temporal and spatial scales, recognized by others as an important focus for SOM model development (Manzoni and Porporato, 2009). Testing across scales is necessary to determine if the added complexity of explicit microbial mechanisms leads to an improvement in SOM simulations. The degree to which specific microbial mechanisms are integrated into SOM models will likely depend on the scale at which a given model is being applied (Stockmann et al., 2013).

2.3.2 First order model versus saturation kinetics

As shown (Figure 2-1, A & B) and discussed both above and in Section 2.3.5, single and multi-pool 1st order decomposition kinetics are commonly used to simulate SOM dynamics. This simple approach performs reasonably well across a diversity of soils and land use changes (Paustian, 1994). Mathematically, however, 1st order kinetics implies a linear proportional relationship between OM inputs and the quantity of SOM stocks when a soils system is at equilibrium (Eqn's 2 & 3). This is a reasonable mathematical approach for some theorized mechanisms of SOM stabilization. The zonal structure theory of organo-mineral interactions is one example, suggesting the thickness of OM layers in the kinetic zones of organo-mineral complexes are predominantly determined by OM inputs (Kleber et al., 2007). However, field research repeatedly demonstrates the capacity for soils to become saturated,

in which case SOM stocks become relatively insensitive to increases in OM inputs or show a diminishing rate of SOM accumulation with increasing rates of OM input (Gulde et al., 2008; K. Paustian et al., 1997; Stewart et al., 2007). First-order kinetics may therefore overestimate OM gains in soils where SOM storage capacity is near a saturation point (Figure 2-2), i.e., where the rate of OM input into a pool may be controlled by the quantity already contained in the pool relative to its maximum holding capacity (Figure 2-1, D) (Hassink and Whitmore, 1997). Given the possibility of land use changes that lead to high OM inputs—such as fertilized, highly productive crops—and given interest in increasing soil C storage as a strategy to reduce atmospheric C concentrations (Follett et al., 2012), the potential for soil saturation is an important consideration as setting an upper limit to SOM stabilization (Baldock and Skjemstad, 2000). In the past this subject was given extensive review (Six et al., 2002). In this section we will update this review with advances in understanding and recent applications in SOM models.

In the Six et al. (2002) review, the three ‘standard’ categories of SOM stabilization mentioned in 2.3.1 were used, of mineral-associations (termed ‘chemical protection’), physical protection through aggregate compartmentalization, and protection through inherent recalcitrance of SOM (termed ‘biochemical protection’), with the remaining OM in the ‘unprotected’ pool. These pools were then linked to measurable SOM fractions in order to evaluate the potential for saturation within each fraction, as well as link these mechanisms to a maximum capacity for total SOM protection (Six et al., 2002). The ‘biochemically protected’ conceptual pool and its associated acid hydrolysis-based measurements have been largely dropped from studies evaluating saturation kinetics. However, the potential for saturation kinetics to affect both bulk soil OM storage as well as dynamics between mineral-associated, aggregate protected, and unprotected OM fractions in soils have continued to be developed and recognized as an important consideration in recent research on SOM and stabilization (Dungait et al., 2012).

Several key studies following the Six et al. (2002) review supported the SOM saturation concept and laid more of the groundwork for its current application. In bulk soils, for example, studies of long-term agricultural experimental sites confirmed the possibility of soil saturation behavior and suggest a distinction between the absolute maximum capacity of soils to stabilize C versus a soil's 'effective stabilization capacity', given external factors such as disturbance by tillage (Balesdent et al., 2000; Stewart et al., 2007). A subsequent laboratory incubation study of soils that varied in their 'saturation deficit' (i.e., proximity to a texture-dependent maximum SOC content), showed that 'saturation deficit' impacted total SOC stabilized with increasing C inputs. This study supported saturation behavior as impacting the total SOM stabilization capacity of soils, and further suggested that management practices to increase SOM storage in soils should target soils with greater starting SOM deficits (Stewart et al., 2008a). Several studies used the Six et al. (2002) framework to show that soil fractions could be evaluated for saturation behavior (Stewart et al., 2009, 2008b). Another study used an alternative measurement approach to evaluate physically separated fractions (e.g. macro and micro aggregates vs. silt- and clay- associated OM), and suggested the possibility of a hierarchy in SOM saturation across mineral-associated and aggregate-protected OM, increasing OM concentrations in more labile, faster cycling fractions when stable fractions are saturated (Gulde et al., 2008). These latter studies suggest that fractions within soils can become saturated even if bulk soils are not, with consequences for how SOM is distributed between pools that vary in turnover times.

The saturation concept has continued to be incorporated into studies of bulk soil OM dynamics. For example, bulk soils have continued to be evaluated for linear versus non-linear relationships between experimental OM additions and SOM content, in order to determine how close experimental soils are to their saturation capacity (Heitkamp et al., 2012; W. J. Zhang et al., 2010). A laboratory incubation study analyzing a gradient of degraded agricultural soils showed that, counter to Stewart et al. (2008a), the greatest C gains were in soils with intermediate rather than maximum saturation deficits

due to destruction of OM storage capacity in the most degraded soils. In this study researchers suggest management practices to increase OM storage need to intervene before soils reach a degradation threshold when stabilization mechanisms begin to decline (Kimetu et al., 2009).

The use of physically separated soil fractions to evaluate mineral –associated, aggregate protected, and ‘unprotected’ OM applied by Gulde et al. (2008) also continues to be a useful conceptual and measurement protocol in current research. One study linked soil C saturation theory to mineral N dynamics and potential for saturation, highlighting concern for mechanisms that saturate stable OM pools and concentrate OM in the more labile OM pools that are at greater risk for loss (Castellano et al., 2012). Another study of long-term agricultural experiments in Virginia uses a similar framework to show saturation in the silt+clay fraction, suggesting further OM accumulation at these sites will occur in particulate organic matter (POM) and aggregates and be more susceptible to loss unless management practices continuously minimize soil disturbance (Stewart et al., 2012). A recent study expands the mineral-associated fraction from only considering the saturation capacity of silt+clay to also include the saturation capacity of Fe and Al oxides. In some soils, such as the Andisols reviewed in the study, aluminum and iron oxides may contribute more to SOM stabilization than clay, therefore should be evaluated for saturation behavior (Matus et al., 2014).

In summary, experimental data increasingly support saturation kinetics as an important mechanism in SOM dynamics, particularly in soils with high SOM and/or increasingly high OM inputs. Therefore, saturation is conceptually well defined, well supported by experiment evidence, and simple (on its own) to express mathematically. It is notable, then, that saturation kinetics have had limited incorporation in SOM models since the Six et al. (2002) review. In one study exploring changes to the RothC-26.3 model to simulate physical protection with aggregate formation and hierarchy, saturation kinetics were not included but suggested as an improvement to include non-linear relationship between fresh organic matter and SOC dynamics (Malamoud et al., 2009). Another study with the RothC model

did add simulation of C saturation, in order improve simulation of high OM input treatments that deviated increasingly from model predictions based on 1st order kinetics. However, the modified model performed poorly for all treatments except those exhibiting saturation behavior, suggesting the need for better implementation of saturation dynamics within the model (Heitkamp et al., 2012).

In conclusion, this is a clear area in need of development in SOM modeling. At the very least, high OM soils in systems with high OM inputs should be recognized as vulnerable to overestimation of SOM storage and accumulation when simulated with conventional first-order decay SOM models.

2.3.3 Temperature controls on decomposition

Temperature is an important driver of SOM dynamics, recognized alongside moisture as key components of climate as a soil-forming factor (Eqn. 1, Jenny, 1941). This fact is neither new nor in dispute. However, in the last two decades controversy and debate have surrounded how, exactly, SOM dynamics respond to temperature change, motivated by the importance of understanding whether soils will become a stronger sink or source of CO₂ as temperatures increase under global climate change (Kirschbaum, 1995; Trumbore et al., 1996). Soils contain far more C than the atmosphere. Even a small percentage change in SOC with increasing temperatures can have a substantial impact on atmospheric CO₂ concentrations. However, the linkages between SOM dynamics and temperature-sensitive soil processes remain poorly understood. Behaviors observed in controlled laboratory incubations are often less consistent or less discernible under more realist *in situ* experiments. Temperature sensitivity is also extremely difficult to isolate from confounding effects of moisture and plant productivity in large scale analyses (Kirschbaum, 2000). While SOM temperature responses are far from resolved, in this section we will present the basis of past debate as well as summarize progress in the context of SOM model development.

First we will clarify our use of the terms ‘temperature response’ and ‘temperature sensitivity’.

Temperature response is a general term referring to changes in a unit of measure (CO₂ flux, mean

resident time, etc.) over a range of incrementally increasing or decreasing temperatures. **Temperature sensitivity** refers to the *magnitude of the response* given the *magnitude of the change*, and is often used as a comparative term. For example, two soils incubated at the same interval of increasing temperatures might both have a positive temperature response and release more CO₂ per unit of temperature, but the magnitude of the increase in CO₂ released per temperature increment is greater in the second soil (e.g. Figure 2-3, R₂) than the first (e.g. Figure 2-3, R₁). The second soil (R₂) therefore has higher temperature sensitivity. Temperature responses are often exponential, so a common term used to express experimental differences in temperature sensitivity (as well as model temperature responses in SOM decomposition) is **Q₁₀**, or the proportional change in respiration with 10° Celsius change in temperature. A Q₁₀ of ~2 (i.e. a doubling of respiration with 10° C temperature increase) is common across biologically meaningful temperatures, but values can vary from less than 0.5 to more than 300 and differ across soil fractions (Hamdi et al., 2013; Leifeld and Fuhrer, 2005). An Arrhenius type equation (Eqn. 4) and a modified version referred to as the Lloyd and Taylor equation (Eqn. 5) are both also common approaches to modeling temperature effects on respiration, connecting temperature effects to the activation energy of chemical reactions (Lloyd and Taylor, 1994). In these equations the rate of respiration given temperature, $R(T)$ is calculated using the general structure of either;

$$R(T) = de^{E_a T^{-1}}, \text{ or} \tag{Eqn 4}$$

$$R(T) = de^{E_a(b+T)^{-1}}, \tag{Eqn 5}$$

where d is a constant, E_a is the activation energy, and b is a parameter used to correct temperature bias.

A central challenge in this area of research is disentangling the abundance of known and suspected temperature responses across the multitude of interacting processes that affect SOM dynamics. At a small scale, for example, many microbial decomposition processes are understood to be temperature sensitive, ranging from the strong temperature sensitivity of enzyme kinetics to potential

temperature sensitivities of microbial growth and substrate use efficiency (Frey et al., 2013; Hagerty et al., 2014). Microbes can also acclimatize or change community characteristics under varying temperature environments through time (Luo *et al.*, 2001, Figure 2-4). The soil matrix can further modulate temperature responses, for example by affecting soil water dynamics or directly interacting with and suppressing microbial enzyme activity. The temperature sensitivity of decomposition also potentially varies by the chemical nature of the SOM substrate being decomposed (Davidson and Janssens, 2006), although as will be discussed this is an area of extensive debate.

On longer timescales and at a landscape level, other factors vary with temperature and cause difficulty with conclusively identifying temperature-related SOM mechanisms. For example, temperature responses of primary productivity occurs over short and long timeframes- e.g. immediate impacts on photosynthesis and transpiration as well as potential long-term impacts on vegetation structure and community dynamics. Primary production responses affect litter inputs into soils as well as soil water dynamics and the decomposition environment experienced by microbes (Bardgett et al., 2008). Ultimately, small-scale, isolated temperature responses and sensitivities in SOM dynamics may have a positive, negative, or no feedback with other ecosystem components in the soil environment when integrated over longer time scales, larger areas, or in interaction with other factors (Figure 2-4).

In this context, experimental results and SOM models are often combined to explore potential impacts of individual mechanisms, with an eye towards understanding global SOM changes with increasing temperatures (Jones et al., 2003; Kirschbaum, 1995). As a consequence, the underlying conceptual model of SOM structure then becomes the foundation on which mechanistic understanding of temperature responses are integrated and applied to larger scales. As will be presented below, this can result in the same data supporting opposite SOM responses to temperature increases. Advances in the understanding of SOM persistence (discussed in Section 2.3.1), have also led to re-interpretation of

some linkages between observed temperature responses and mechanisms within SOM models. The remainder of this section will focus on these developments.

Since the topic emerged, concern with SOM responses to global warming focused research on evaluating temperature sensitivities across temperature ranges in bulk soils as well as among individual SOM fractions with different turnover rates (i.e. 'labile' versus 'recalcitrant' SOM). Ecosystem models supported the potential for increasing temperatures to increase C inputs into soils via the stimulation of decomposition rates, particularly by increasing the release of mineral N (Schimel et al., 1994). An early synthesis of incubation studies noted variability in Q_{10} values that suggested greater sensitivity of SOM responses at lower temperatures, which could place the large stores of SOM in cold boreal and arctic regions at greater risk for loss (Kirschbaum, 1995). A different study using repeated measures of soils across an elevation transect showed that more 'labile' SOM could contribute to rapid SOM response with temperature increases (Trumbore et al., 1996), but that longer term consequences are of greater concern for the often larger pool of SOM cycling more slowly.

Several topics then became subject to extensive debate, one centered on the hypothesis that 'labile' and 'recalcitrant' SOM fractions had different temperature sensitivities, with the latter being more sensitive than the former. At the time, this hypothesis was connected to a model linking SOM substrate quality to temperature sensitivity of decomposition. This model, now referred to as the carbon quality-temperature theory (Fierer et al., 2005), was based on the hypothesis that SOM decomposition dynamics were determined by substrate quality via the number of enzymatic steps- and therefore the total free energy change- required to mineralize organic matter carbon. The carbon quality-temperature theory predicted greater temperature sensitivity in low quality substrates compared to high quality substrates, as well as greater temperature sensitivity at low temperatures versus high temperatures (Bosatta and Ågren, 1999). Based on the assumption that 'old' SOM is more chemically complex and a poorer microbial substrate than 'new' SOM, this made a logical linkage to the

hypothesis that ‘older’ (i.e. more stable, ‘recalcitrant’) SOM will be more sensitive to temperature than ‘newer’ (i.e. less stable, ‘labile’) SOM. Liski et al (1999) then explicitly argued against this hypothesis, presenting results that suggested old SOM is *less* temperature sensitive than newer litter, leading to less C loss and even some C gain with increasing temperatures than predicted by other models (Liski et al., 1999). However, the SOM model underlying Liski et al.’s (1999) conclusions was criticized, specifically the assumption of fixed residence times in the pools used to simulate SOM and temperature effects on respiration (Ågren, 2000). Subsequent studies continued to examine this hypothesis, yielding results that supported, showed no difference, or suggested the opposite relationship between ‘labile’ versus ‘recalcitrant’ SOM, maintaining a high level of uncertainty on this topic (Benbi et al., 2014; Conant et al., 2008; Fang et al., 2005; Hartley and Ineson, 2008; Melillo et al., 2002). This theory has been argued as largely irrelevant for mineral-associated SOM and SOM that is cycling more slowly. As discussed in Section 2.3.1, ‘recalcitrance’ does not have a basis in chemical complexity (Kleber, 2010), and older SOM is not necessarily more thermodynamically stable or chemically different than ‘newer’ SOM (Kleber et al., 2011). The activation energy-based temperature sensitivity in the carbon quality-temperature theory, therefore, is not necessarily a mechanism with logical application to mineral-associated or slowly cycling OM pools (Conant et al., 2011). However, it should be noted a study that looked to address the shortfall of short-term incubation studies in the comparison of ‘labile’ and ‘stable’ SOM temperature sensitivities—specifically by evaluating initial versus final soils from long-term bare fallow agricultural experiments, where labile SOM has been shown to be progressively depleted through time—used *apparent* activation energy as part of strong evidence supporting greater temperature sensitivity in more stable SOM (Lefèvre et al., 2014).

A second topic of controversy in temperature effects on SOM emerged from a study that questioned the temperature sensitivity of mineral soils as a whole, suggesting they are largely insensitive to temperature and therefore may not be as important in the context of climate change as

hypothesized at that time. This study based their conclusions on experimental results from mineral soils in temperate forested systems (Giardina and Ryan, 2000). A theoretical model exploring the separation of physico-chemical stabilization (e.g. stabilization by adsorption to soil minerals) from microbial processes was able to replicate this effect simulating SOM at equilibrium, if physico-chemical stabilization increased in excess of microbial respiration (Thornley and Cannell, 2001). However, as with the Liski et al. (1999) study, results from Giardina & Ryan (2000) were also critiqued on the basis of the underlying SOM model, which in this case made the assumption of using single SOM pool model to calculate turnover times. It was suggested that a multi-pool SOM modeling approach was needed to calculate turnover times, to prevent obscuring temperature sensitivities of individual SOM pools (Davidson et al., 2000; Powlson, 2005). The Giardina & Ryan (2000) data were eventually re-analyzed by Knorr et al. (2005) using a multi-pool approach, which showed that cumulative temperature insensitivity in the short term *could* be exhibited by aggregating responses of individually temperature-sensitive SOC pools, but ultimately would lead to a strong positive feedback in the long term as more slowly cycling pools persist in releasing CO₂. This reverses the conclusion from Giardina & Ryan (2000) and fell in line with other studies, by supporting a strongly positive feedback between warming and SOM decomposition in mineral soils. However, Reichstein et al. (2005) recommended precaution towards the Knorr et al. (2005) conclusions. Though they supported the use of the multi-pool approach, Reichstein et al. (2005) noted that Knorr et al.'s (2005) results—showing that slowly cycling SOM is more sensitive to temperature than more rapidly cycling SOM—could be due to a statistical anomaly (Reichstein et al., 2005).

Even as research has moved past these earlier controversies, identifying mechanistic linkages between SOM dynamics and temperature remain a challenging experimental effort. As mentioned earlier, it is difficult to isolate temperature-sensitive mechanisms in SOM dynamics, particularly across scales and within slowly cycling SOM pools. It has been suggested that the latter is in part due to the

relatively short duration of most climate change experiments (Conant et al., 2011). Regardless, evidence for positive feedbacks between increasing temperatures and SOM is often strongest with incubation studies due to minimization of confounding effects, such as concurrent changes in primary productivity (Janssens et al., 2001). At larger scales temperature sensitivity often seems reduced, suggesting a weaker or slower positive feedback between warming temperatures, SOM, and atmospheric CO₂ (Ise and Moorcroft, 2006; Kirschbaum, 2000). One large scale study did support a linkage between SOM loss and warming climate conditions through direct measurements at a national scale, although they were not able to distinguish loss through respiration versus loss through leaching (Bellamy et al., 2005). In their highly cited review on the topic, Davidson and Janssens (2006) highlight the relative ease with which environmental factors can obscure temperature sensitivities, suggesting separation between ‘intrinsic’ and ‘apparent’ temperature sensitivity due to the interaction with environmental constraints that could amplify or suppress temperature responses. Ecosystem respiration has shown a strong convergence in ‘intrinsic’ temperature sensitivity when high resolution FLUXNET CO₂ data were used to exclude confounding ecosystem properties and seasonal dynamics (Mahecha et al., 2010). However, this analysis also suggested mechanisms that impact C stabilization versus C supply—operating both above- and belowground on longer time scales—may potentially have complex impacts on ecosystem respiration and C cycling behavior (Mahecha et al., 2010). Studies support the potential for increased rates of C cycling in soils under increasing temperature, but the resulting impact on SOM storage remains uncertain (Bond-Lamberty and Thomson, 2010; Giardina et al., 2014; Smith and Fang, 2010). Cumulatively these studies support the importance of identifying mechanisms that drive SOM responses to warming temperatures, as well as incorporating these mechanisms explicitly into SOM models.

Many widely used SOM models cannot easily reflect specific temperature-sensitive mechanisms, due to their basis on kinetically-defined SOC pools that are not clearly linked to measurable soil fractions (Dungait et al., 2012). Representations of temperature controls on decomposition within these models,

and the data used to inform them, must therefore be considered carefully. For example, many widely used models initially had their temperature functions parameterized using incubation data. Examples include the CENTURY and the RothC models (Jenkinson and Rayner, 1977; Kirschbaum, 1995; Parton, 1987). These models have obviously undergone considerable change and development since initial parameterization (e.g. Del Grosso *et al.*, 2005). However, given observations that temperature sensitivity tends to change in strength across spatial scales (e.g. Kirschbaum, 2000; Ise & Moorcroft, 2006), incubation-based model parameterizations of temperature response should be examined carefully when models are applied at larger scales. Additionally kinetically-based SOC models are commonly implemented in Earth System Models (ESMs), often using Q_{10} functions to simulate temperature sensitivity (Todd-Brown *et al.*, 2013). Q_{10} functions have been shown to perform poorly at temperature extremes, making this approach potentially poorly suited to simulate tropical and arctic ecosystems where climate change is of particular concern (e.g. Koven *et al.*, 2011). The use of a static Q_{10} function has also been strongly criticized (Davidson *et al.*, 2006; Tang and Riley, 2015). A Gaussian model has been suggested as a better representation of temperature sensitivity across a wider range of temperatures (Tuomi *et al.*, 2008). Using multiple temperature response models for measured-modeled comparison can also be more revealing than the use of a single model (Benbi *et al.*, 2014). Implementing functions to better simulate temperature sensitivity in SOM models based on kinetically-defined SOC pools, as well parameterizing temperature sensitivity across scales, is a logical and reasonably straightforward area to improve SOM model development. However kinetically-defined models will always be limited by the lack of mechanistic linkages between SOM dynamics and temperature response, by the inability to link SOC pools to mechanistically defined and measurable SOC fractions.

As an alternative, researchers are beginning to develop and explore models to simulate temperature-sensitive respiration responses more mechanistically, based on understanding of factors such as substrate diffusion, enzyme activity, and membrane transport (Davidson *et al.*, 2006). The

DAMM model, as one example, simulates the interaction between soil water, soluble substrates and temperature as they affect enzyme kinetics (Davidson et al., 2012). Other models like *ecosys* are better suited to accommodate mechanistically-based microbial responses to temperature, by explicitly simulating microbial communities (Grant et al., 2003). The substrate quality-based model by Bosatta & Ågren (1999) provides a mechanistic basis for temperature sensitivity in some SOM components. A litter incubation study supported this theory, with results showing increased temperature sensitivity in lower quality litters as well as litters as they progressed through the decomposition process (with declining quality as decomposition advanced) (Fierer et al., 2005). The carbon quality-temperature theory was also supported by an analysis of the low density (or “light fraction”; LF) fraction of soils, a SOM fraction considered to be more microbially accessible as it is not associated with soil minerals (Wagai et al., 2013).

More recent models include better mechanistic linkages to a wider array of SOM pools. One conceptual model differentiates between processes that make SOM available for decomposition (e.g. physical protection and aggregate turnover) versus processes that decompose SOM once it is available (e.g. microbial enzyme dynamics, depolymerization, Figure 2-4) (Conant et al., 2011). Microbial interactions with SOC dynamics under warming scenarios have suggested a diversity of possible pathways for SOM dynamics and interactions with global carbon cycles (Bardgett et al., 2008), and also are being more explicitly incorporated into SOM models. Microbial substrate use efficiency has been shown to be sensitive to temperature, but with the potential for community shifts and acclimation that may reduce this sensitivity through time (Allison et al., 2010; Frey et al., 2013; Luo et al., 2001; Tucker et al., 2013). An incubation study supported a separation of microbial turnover from MGE, with temperature sensitivity of the former and temperature insensitivity in the latter leading to possible increases in SOC with temperature, a dynamic not reflected in current models (Hagerty et al., 2014). A model linking microbial biomass and enzyme kinetics to temperature and moisture aims to tease apart

these tightly linked drivers, supporting field experiment results suggesting moisture control when moisture is limiting, and temperature control when it is not (Steinweg et al., 2012). A recent model suggests CUE and abiotic mechanisms like mineral sorption vary interactively in temperature sensitivity through time, suggesting the need for temperature sensitivity to be modeled dynamically in order to gain greater accuracy through better linkages to underlying processes (Tang and Riley, 2015). Long-term multi-factorial ecosystem-level experiments are needed to clarify interactive climate change effects on microbial processes, and better inform development of these types of models (Bardgett et al., 2008).

In summary, temperature sensitivity in SOM dynamics remains an important area of continued research, both experimentally and from the standpoint of SOM model development. There has been a strong call for greater standardization and clarity in how experimental results are reported and interpreted, to support better integration with modeling efforts (Subke and Bahn, 2010). Models, in turn, need to better reflect the full spectrum of potential temperature responses, in order to more accurately simulate the implications for the timing, magnitude, direction, and geographic location of SOM changes under increasing global temperatures. Only further experimental exploration of temperature-sensitive decomposition mechanisms—particularly including large-scale studies that cross a range of ecosystem types (Giardina et al., 2014; Subke and Bahn, 2010)—integrated with SOM model development will continue advancing this area of research.

2.3.4 Deep soil organic matter dynamics

‘Deep soil’ in this discussion refers to the soils beneath the surface 20-30 cm depth layer, which has often been excluded from many ecosystem-scale models of SOM dynamics. Organic matter dynamics below the top soil layers remain, to a large extent, much less studied and one of the open frontiers in SOM research. Subsurface soils are consequently an important area of development in SOM modeling. Many models focus on the top 20-30 cm soil layer, partially due to logistics; surface soils are easier to sample, are often more uniform (particularly in tilled agricultural soils) and have much more

data available for model formulation and testing. In addition, surface soils generally contain a large fraction of the total SOM, which is younger and cycling more rapidly than SOM in deeper soil layers, and which is most responsive to management perturbations (Batjes, 1996; Jobbagy and Jackson, 2000; Paul et al., 1997; Scharpenseel et al., 1989). This has led to their emphasis in the simulation of ecosystem dynamics and soil responses to land management practices. Historically, SOM in deep soil layers was thought to consist mainly of inert complex humic material and mineral-bound OM. However while mineral-bound OM remains supported as an important stabilization mechanism in subsurface soils (Rumpel and Kögel-Knabner, 2010), more recent analyses show deep SOM to mainly consist of simple molecules—often dominated by highly processed microbial products (Erich et al., 2012)—that are also responsive to land management change (Baker et al., 2007; Follett et al., 2012; Poeplau and Don, 2013; Trumbore et al., 1995), on shorter timescales than previously understood (Koarashi et al., 2012). Therefore there is more recent focus on dynamics of the 50% or greater total SOC contained in soils *below* 20-30cm (Batjes, 1996; Jobbagy and Jackson, 2000), particularly in the context of subsurface soils' role, response, and management under global change scenarios (Salomé et al., 2010). Knowledge gaps in the understanding of deep SOM dynamics, as well as their connection to global cycles, are being targeted by experimental and field research, with calls to better reflect and test new hypotheses in SOM models (Schmidt et al., 2011).

Deep soil OM dynamics involve similar mechanisms to surface soils, but with the potential for time lags and differences in soil environments that may separate subsurface and surface SOM responses to change (Fierer et al., 2003a; Salomé et al., 2010; Sanaullah et al., 2011). A review of deep soil OM by Rumpel & Kögel-Knabner (2010) provides a framework for recent experimental work focusing on deep SOM dynamics. They highlight the need to clarify dominant SOM inputs as well as mechanisms that stabilize or destabilize SOM in deep soil layers. They summarized key inputs to deep SOM as 1) the movement of dissolved organic matter (DOM) with water, 2) root growth, exudates, and turnover, and

3) physical OM transport through bioturbation or physical soil processes. They suggest destabilization mechanisms include aggregate disturbance and increases in microbial access to nutrients and labile C. Stabilization of deep SOM is linked more strongly to mineral associations and the physical separation between dispersed microbes and SOM at depth. However the authors state that the relative importance of these mechanisms as well as their interactions remained in need of development, particularly with *in situ* field experiments (Rumpel and Kögel-Knabner, 2010). Moreover, the relative importance of these factors is likely variable across ecosystems (Jobbagy and Jackson, 2000; Schmidt et al., 2011). In the following section we will summarize recent research in deep SOM, expanding on stabilization and destabilization mechanisms as well as the dynamics of deep SOM inputs. We will then discuss modeling approaches to deep SOM dynamics and conclude with suggestions for future directions.

The importance of physical separation between microbes and OM in deep soils as a stabilization mechanism—specifically as opposed to the inherent chemical complexity of deep SOM—has received widespread experimental support (Rumpel and Kögel-Knabner, 2010; Salomé et al., 2010). For example, a study using ‘bomb’ radiocarbon from past atmospheric thermonuclear testing provided evidence that subsurface SOM can cycle rapidly on a decadal scale, turning over up to an estimated 1.6% of total annual gross terrestrial primary production across temperate grassland and deciduous forest biomes each year (Koarashi et al., 2012). In this study the chemistry of the light fraction, often theoretically used as a measure of fast-cycling SOM, was consistent across depths, only increasing in age but not changing in chemical characteristics (Koarashi et al., 2012). A different field study using ^{13}C and ^{15}N labeled wheat roots buried in litter bags at three soil depths to 90cm observed that the chemical characteristics as well as the quantity of litter decomposed at different depths was similar after a 3-year period (Sanaullah et al., 2011). The importance of physical protection from microbes in subsurface SOM stabilization is further supported by a laboratory incubation demonstrating that old SOM in deep soil layers could be mobilized simply by successive drying and rewetting, suggesting that SOM in deeper soils is not

necessarily biologically inert but rather may persist through mechanisms that limit microbial access (Schimel et al., 2011). The authors of this study suggest the term 'metastable', for deep SOM that is 'unused but not unusable' (pg 1103).

Mechanistic linkages between microbial community characteristics and SOM stability remain poorly understood. Microbes clearly vary across the soil profile, and can show different sensitivities to factors such as temperature, moisture and nutrient addition (Fierer et al., 2003a). Microbes have a strong association with SOC content across soil depths (Fierer et al., 2009, 2003b), and their use of 'old' versus 'new' soil C has been shown to depend on depth as well as microbial community composition (Kramer and Gleixner, 2008). One study demonstrated that microbial communities varied as much across the vertical soil profile as they do between ecosystem in the surface soils, but without being able to link these differences to SOM dynamics (Eilers et al., 2012).

Regardless of mechanistic linkages to microbial community characteristics, the importance of SOM stabilization by physical separation from sparse microbes supports the potential importance of 'priming' as a SOM destabilization mechanism in deep soil layers. Priming occurs when inputs of 'fresh' OM - i.e. labile OM that has not been microbially-processed leads to increasing decomposition of otherwise persistent deep SOM with the stimulation of microbial activity (Fontaine et al., 2007; Kuzyakov et al., 2000). Priming could play an important role in predicting deep soil responses to increasing concentrations of atmospheric CO₂, particularly in forested systems where elevated CO₂ has been shown to increase fine root production as well as cumulative C inputs into deeper soil layers (Iversen, 2010). The potential for priming also must be considered in land management strategies for increasing SOM, particularly with the growth of deep-rooted crop species. Deep soils have the potential to gain and store soil C with land management to increase soil C sequestration (Poeplau and Don, 2013). However, priming may offset desired gains in SOM storage with increased belowground OM inputs (Dungait et al., 2012; Follett et al., 2012). Research aimed towards evaluating priming in deep soils has

not yet identified easily generalizable mechanisms, but rather suggests a high degree of site specificity. For example, Free-Air CO₂ Enrichment sites have shown accrual, loss, as well as no change in SOC from increased OM inputs to deeper soil layers (Drake et al., 2011; Iversen et al., 2012; Langley et al., 2009).

As described earlier there are several pathways for OM to move into deep soil layers, including bioturbation, root growth and turnover, and DOM movement. Of these, DOM has received particular attention. This attention is due to its rapid cycling, as well as its role linking surface OM with deep soil mineral fractions through vertical transport and thereby possibly affecting deep SOM stabilization and storage (Fröberg et al., 2009; Rumpel and Kögel-Knabner, 2010). The quantity and quality of DOM from different parts of the soil profile can also serve as a metric for cumulative behavior of sorption, desorption, decomposition and leaching processes, as they interact with soil minerals, pH, litter, and hydrology (Kalbitz et al., 2000). In earlier research DOM emerging from deeper soil layers were thought to have 'escaped' either adsorption or respiration after generation from litter decomposition (Schiff et al., 1997), an idea supported by bulk DOC measurements across the soil profile (Kalbitz et al., 2000). However more recent evidence supports the concept of repeated microbial processing as DOM is successively sorbed and desorbed down the soil profile, leading to predominance of highly processed DOM as depth increases (Kaiser and Kalbitz, 2012). Drying-rewetting can affect the depth and direction of DOM movement different in surface versus deep soil layers, with the potential for either upward or downward flow depending on the size and frequency of drying and rewetting cycles (Lopez-Sangil et al., 2013). There is strong evidence that Fe- and Al-oxide concentrations have a positive effect on DOM sorption capacity (Oren and Chefetz, 2012; Sanderman et al., 2008). However other mechanisms can affect DOM in deep soil layers. For example N addition decreased DOM release from deep soils in a temperate largely deciduous forested system. The authors linked this behavior to changes the soil chemical environment and solute behavior with the form of N addition (Hagedorn et al., 2012).

Recent research on deep SOM dynamics still only reveals pinpoints of understanding in a complex belowground system. Logistical challenges and lack of data are profoundly limiting. For example the Jobbagy & Jackson (2000) global estimate of SOM cited above required mathematically extrapolating down to 3m from datasets largely limited to 1m depths, excluded all agricultural soils, and discussed the possibility of biome-specific biases due to lack of data (Jobbagy and Jackson, 2000). ‘Deep soil’ research also may often not go deep enough. A study of highly weathered, very deep soil profiles demonstrated that SOC measurements limited to the top 50cm of soil would only capture as little as 14% of total SOC across the soil profile, while even measurements as deep as 5m captured at most 75% of the total in soils that averaged 21m in depth (Harper and Tibbett, 2013). Burial of soils through volcanic, loess, alluvial, or human mechanisms can create pockets of deep SOM with characteristics and behavior largely unaccounted in either global estimates or existing deep SOM model dynamics (Chaopricha and Marín-Spiotta, 2014). In this context, perhaps even more so than in other areas of SOM research, SOM model-data integration is needed to advance understanding. Simulation models can provide a framework to integrate data and test hypotheses, potentially helping direct subsequent experimental work to tease apart interacting, often co-occurring mechanisms in deep soil environments.

In the past, deep soil SOM turnover was only explicitly included in a few models and was noted as a critical area for SOM model development (Falloon & Smith, 2000). In addition to different approaches to addressing the three main deep SOM inputs summarized by Rumpel and Kögel-Knabner (2010)—roots and exudates, SOM movement with water, and vertical mixing with bioturbation and other physical processes—models developed before and since use a variety of approaches to simulate changing dynamics and SOM stability across soil layers. As one example, the DAYCENT model—a newer version of the CENTURY model—was modified to simulate deep soil C dynamics only by slowing SOM pool turnover and increasing allocation to passive soil C, without separating soil layers (Wieder et al., 2014b). Alternatively the Community Land Model (CLM) was modified to simulate deep SOM dynamics

using a vertical cascade, where SOM passes through layers in the soil profile with loss at each transition (Koven et al., 2013). The vertical cascade approach and multiple soil layers is more common (Table 2-2). The SOLVEG-II model, for example, uses 27 separate layers from the surface to 5.5m, each individually containing three CENTURY-type first order kinetic SOM pools with flows between preceding and following layers (Ota et al., 2013).

As discussed earlier, DOM is clearly an important mechanism of OM input into deep soil layers, and recent models have varied in explicitly or implicitly simulating DOM movement (Table 2-2). The RothPC-1 model, for example, includes DOC implicitly by modeling vertical C transport associated with advection (distance time⁻¹) (Jenkinson and Coleman, 2008). The DyDOC model, on the other hand, explicitly models DOC dynamics across soil layers using measured soil C pools derived from a detailed ¹⁴C labeling experiment (the Enriched Background Isotope Study (EBIS) out of Oak Ridge Reservation (Tipping et al., 2012). However the DyDOC model does not include the exchange of C with solid soil C, suggested by other researchers as a mechanism to explain both greater age and greater microbial processing of OM at deeper soil depths (Kaiser and Kalbitz, 2012; Sanderman et al., 2008). The SOVEG-II model is another model that explicitly simulates DOM, as a function diffusion, advection with water flow, plant uptake, and microbial decomposition (Ota et al., 2013). Alternatively, in the SOMPROF model DOM is implicitly simulated using a single advection rate (Braakhekke et al., 2013).

We would like to note that root inputs and bioturbation show much less variation in modeling approaches than DOM. Root distributions with depth tend to be modeled using exponential functions (Table 2-2). Modeling approaches to roots has been critiqued as insufficient to capture key dynamics, with the suggestion of modifying models to accept root distribution data directly (Iversen, 2010). Limited study of deep root dynamics is largely linked to the logistical challenges of their measurement and evaluation (Maeght et al., 2013). The limited exploration of modeling approaches to root growth in SOM models is likely a combination of the lack of data with the potential complexity involved in moving

away from a simple exponential function. However vertical root dynamics are certainly important in the context of projecting SOM responses with climate change (Iversen, 2010). Therefore as deep SOM modeling approaches develop, this is an area in need of careful consideration. Bioturbation, on the other hand, has been shown to be largely inconsequential compared to other input and transport mechanisms (Braakhekke et al., 2013). It is therefore less of a priority for deep SOM model development.

The goal of these various modeling approaches to deep SOM is to clarify key mechanisms, identify patterns, and ideally simulate impacts of future climate projections and land use change scenarios with some degree of accuracy. The C-TOOL model takes a practical approach to its application, by simplifying assumptions and solely focusing on whole-soil SOC dynamics in agricultural systems. The C-TOOL model aims to encourage utility by minimizing parameters and data requirements for its use, and saw reasonable model performance when initial SOM pools were optimized using measured data (Taghizadeh-Toosi et al., 2014). In a study by Guenet et al. (2013), simplicity was also the aim, by comparing simple models that simulate vertical SOM transport using either only diffusion, only advection, or the combination of diffusion and advection as they acted on three different SOC mineralization models (1st order kinetics, only the input of fresh OM, or 2-pool 1st order kinetics) (Guenet et al., 2013). In this study the vertical transport mechanism with the best fit to data from a long-term bare fallow experiment depended on the underlying SOC model, yielding little mechanistic understanding for transport but supporting the importance of fresh SOC inputs in controlling deep soil OM dynamics (Guenet et al., 2013). Other experimental results are supported by model simulations. Numerical experimentation of rooting depth using the SOLVEG-II model resulted in SOM movement below rooting depth as well as dominance of SOM in active and slow pools at depth (Ota et al., 2013). These results confirm both as possible mechanisms leading to global observations of SOM below rooting depths (Jobbagy and Jackson, 2000), as well as supporting observations that deep SOM can cycle on

decadal scales (Koarashi et al., 2012). The BAMS1 model, which takes a more mechanistic approach to SOM and includes vertical SOM dynamics, simulated the persistence of relatively decomposable SOM across the soil profile. This model has potential to test SOM responses to global change across the soil profile. However it is highly complex and requires expanded observed data to more carefully test components of the model's internal structure (Riley et al., 2014).

Clearly there is room for iterative development of deep SOM understanding by combining experimental, field, and modeling research. We would like to note that, given the preceding short review, changes in temperature sensitivity and response to climate change are particularly poorly understood across soil depths, are not accounted in these models, and are an area in need of targeted consideration (Subke and Bahn, 2010). The models discussed in this deep soil review support some observed mechanisms but also suggest testable hypotheses in need of additional data to confirm or refute. Carbon isotope labeling and tracers are particularly important tools for deep SOM research, by allowing for OM dynamics to be observed with minimal disturbance. However there is likely value in using other, non-carbon tracers with known dynamics and interactions with SOM. For example, the use of $^{210}\text{Pb}_{\text{ex}}$ was able to inform SOMPROF model parameters, although use in addition with ^{14}C or other C labeling was suggested as a more powerful approach (Braakhekke et al., 2013). Given logistical challenges in studying the deep soil realm, collaborative efforts between modelers and experimental researchers are needed identify, understand, evaluate, and predict deep SOM dynamics.

2.3.5 Representation of SOM in earth system models (ESMs)

The development of SOM modeling within Earth System Models (ESMs) is an advancing area of research in need of careful attention from soil scientists. Soils contain the largest terrestrial C pool, and have the potential to be either a sink or source of atmospheric greenhouse gas (GHG) emissions due to interacting factors that vary across scales, ranging from global vegetation shifts, to site-specific land management practices, to temperature effects on microbial dynamics (e.g. Section 2.3.3) (Heimann and

Reichstein, 2008). The integration of SOM models into ESMs is a critical activity for the robust characterization of feedbacks between the Earth System and future climate changes, both for the purposes of mitigation and adaptation across multiple fields that include the sciences, economics, and policy. However the inclusion of SOM models in ESMs present new challenges in SOM model development and validation, due to high uncertainty, variability, and uneven coverage in both data needed to drive SOM models and data to evaluate model performance. The use of SOM models within ESMs also requires SOM researchers to grapple with the challenge of integrating the understanding of SOM dynamics across scales (Manzoni and Porporato, 2009). Model intercomparison, benchmarking, and model-data integration projects will be an increasingly important component of scientific development in this field (Luo et al., 2012). In this section we will describe the development of SOM modeling in ESMs, and summarize current focal areas within ESM model development as well as across multi-model ESM comparisons

Global biotic C cycling components included in ESMs are often grouped in three broad categories: atmosphere, land, and ocean. As the largest terrestrial C pool (Jobbagy and Jackson, 2000), as well as by interacting dynamically with atmospheric C, soils play an important role in determining global land-based C cycling and land-atmosphere C interactions. Models of SOM are accordingly needed in ESM development to dynamically link atmospheric C, climate change effects, and land-based C storage (Falloon and Smith, 2000; William R. Wieder et al., 2014).

Earth system models are highly computationally intensive but have been developed to increase their resolution and complexity as advancing technology allowed more detailed climate modeling coupled with feedbacks from biotic and abiotic system components. ESM development began in the 1960s, but originally only included static land surface simulations to gain limited capacity in simulating water runoff and evaporation. Land surface models eventually became more dynamic, interacting with the atmosphere in model simulations. However dynamic C cycling did not appear until the 1990's, with

the advancement of simulating primary productivity in ESMs through a more mechanistic understanding of photosynthesis and stomatal conductance (e.g. implementing the model from Farquhar *et al.* (1980)). This created a dynamic linkage between the atmospheric C cycle and net primary productivity (NPP) of the biosphere, which then made C available to move through other ecosystem processes (e.g. growth in different vegetation structures, litter inputs, soil decomposition) (Pitman, 2003). For the sake of simplicity, initially ESMs did not include coupled feedbacks between climate and terrestrial C cycling, but instead simulated climate change effects on soils separately from climate change forecasting models (Jenkinson *et al.*, 1991; Schimel *et al.*, 1994). However the need to couple soil models with both climate and vegetation models was well recognized (Jenkinson *et al.*, 1991).

When coupled atmospheric and terrestrial C cycling models did develop, the resulting predictions suggested the potential for soils to accelerate climate change (Friedlingstein *et al.*, 2001). These predictions were largely driven by relatively simplistic approaches to terrestrial C cycling, wherein the effects of increased CO₂ concentrations on photosynthesis surpassed temperature effects on microbial respiration (Cox *et al.*, 2000), with high uncertainty in the latter (Jones *et al.*, 2003). Subsequent ESM simulations and multi-model comparisons included some form of SOM modeling, varying by the number of soil pools being modeled but generally using 1st order kinetics (Section 2.2, Figure 2-1) (Friedlingstein *et al.*, 2006; Krinner *et al.*, 2005; Sitch *et al.*, 2003). ESMs have since been developed to link C and N cycling (long-recognized as an important component for global SOM modeling (Schimel *et al.*, 1994)) as well as the simulation of land use and land cover changes (LULCC) with climate change (Friedlingstein and Prentice, 2010; Lawrence *et al.*, 2011; Wang *et al.*, 2013).

Feedbacks between nutrient cycles at global scales continue to be an important area of development in ESMs. For example, a terrestrial coupled C-N model emphasized the importance of including demand-driven biological N fixation to more accurately simulate C-N interactions in terrestrial systems at a global scale (Esser *et al.*, 2011). Another study highlighted phosphorous (P) dynamics,

particularly in P-limited tropical ecosystems, as an important component missing from most global models (Yang et al., 2014). Spin-up simulations to initialize C pools within ESMs also remain a major bottleneck in the implementation of more complex SOM models, although there is ongoing work to decrease the computational intensity of this component of ESM simulations (Wang et al., 2013; Xia et al., 2012). In one study, global SOM model simulations have been shown to improve with the use of observed rather than internally simulated litter decomposition, with some models showing convergence over long-term projections with climate change impacts (William R. Wieder et al., 2014). More recently, ESMs have been developed to include soil C and N cycling in deeper soil layers (discussed in Section 2.3.4), which while not capturing SOC age dynamics adequately, did improve long-term simulations of SOC responses to climate change (Koven et al., 2013).

As ESMs advance and incorporate SOM models with higher levels of complexity, there are expanding opportunities to implement and test of new ideas in SOM modeling, including many discussed earlier in this chapter. Clearly the debate surrounding SOM dynamics under increasing temperatures, discussed in Section 2.3.3, can and should link to ESM simulations both for hypothesis testing as well as improving ESM simulations under climate change scenarios. The implicit versus explicit inclusion of microbial biomass and processes, discussed in Section 2.3.1, is another example. As mentioned above, 1st order kinetic SOM models remain widely used in ESMs. However microbial dynamics have many direct and indirect linkages to land-atmosphere carbon exchange, with complex interactions and potential for community shifts that can lead to positive or negative atmospheric feedbacks (Allison et al., 2010; Bardgett et al., 2008; He et al., 2010). The implicit inclusion of microbial processes that dominate ESMs has been criticized (Schimel, 2013), with arguments that microbial growth efficiency (MGE) controls on SOM dynamics (Wieder et al., 2013; Xu et al., 2014), as well as explicit microbial biomass and microbial C:N stoichiometry would improve model predictions (Fujita et al., 2014; Todd-Brown et al., 2012). Simulating MGE did improve global simulations of measured SOC

variability despite poor performance in tropical and Arctic ecosystems (Wieder et al., 2013). Incorporating microbial dynamics in the Community Land Model (CLM) also changed global projections of SOC dynamics with warming temperatures and increased C inputs from CO₂ fertilization on plant growth, resulting in larger SOC loss from the former and minimal SOC gain from the latter as compared with prior ESM projections (Wieder et al., 2013). However adding an explicit microbial biomass pool to ESMs remains a challenge, in terms of both model complexity and data availability. For example, globally scaled distributions of microbial biomass that could be used to inform or test ESM predictions have only recently been estimated and were derived from highly variable global data unevenly distributed across biomes and hemispheres (Serna-Chavez et al., 2013; Xu et al., 2013). It has been suggested that SOM models incorporating more mechanistic approaches to microbial processes may be better suited to capture transient change in large-scale ESM simulations (Manzoni and Porporato, 2009; Schimel, 2013). There is certainly appeal to the use of microbial enzyme kinetics and stoichiometric constraints to derive a better, simpler 'first principles' approach to SOM dynamics that is analytically tractable and might emulate the early success of simulating photosynthesis and stomatal conductance in ESMs (Bonan et al., 2012; Davidson et al., 2014; Pitman, 2003). However these types of models (e.g. the DAMM model) are still in the early stages of development and testing.

Ultimately, ESMs pose a central challenge to SOM modeling and model development: that is, they test the ability of SOM models to predict accurately across temporal and spatial scales. This arises from both the varying scale of ESM application—e.g. short to long term past and future projections across regional to global spatial scale—as well as the varying scale of the processes and the data used to develop, run, and evaluate simulations (Ostle et al., 2009). Integrating SOM research from smaller-scale experimental studies and model development into coupled global models (e.g. dynamic global vegetation models, (Arneth et al., 2009)) that can then link to ESMs requires determining how best to scale up in spatial resolution while scaling down and simplifying model processes as much as is required

(Figure 2- 5). Deciding how best to integrate any of these components across varying process complexities and spatial scales remains difficult. Early analyses showed that while simple versus more complex SOM models in ESMs converged over long periods of time, the complex models more accurately captured transient changes (Schimel et al., 1994). More recently, the relative uniformity in using 1st order kinetics SOM modeling in ESMs has been shown to result in better performance at large temporal and spatial scales, but poorer performance at smaller scales due to either poor data availability, high levels of uncertainty, or poor representation of ecosystem properties/dynamics important to capture finer-scale dynamics (Todd-Brown et al., 2013). It still remains unclear whether explicit modeling of microbial biomass and processes instead of using 1st order kinetic SOM modeling approaches in ESMs lead to improvement in predictive accuracy across scales (Todd-Brown et al., 2012).

Answering these questions requires multi-model ESM performance comparison with validation datasets that range from regional to global scales, a need that has been recognized but remains in early developmental stages (Luo et al., 2012). For example, data from the C4MIP multi-model comparison suggest the potential for increased C storage in high northern latitudes due to increased primary production and rates of litter turnover, but recognizes that these estimations are missing a substantial list of potentially important interactive factors (e.g. C in permafrost and peatlands, impacts of land use disturbance, N cycling) (Qian et al., 2010). Multi-model comparisons (Cramer et al., 2001; Friedlingstein et al., 2006; Qian et al., 2010) and simulations that interchange key submodels to test model sensitivity have been a useful tool for ESM development (Meehl et al., 2004). As a high profile example, the Intergovernmental Panel on Climate Change (IPCC) developed ensembles of Earth system Models of Intermediate Complexity (EMICs) for a more robust approach to simulate past and future climate change (Randall et al., 2007). SOM model development could continue to benefit from involvement in these efforts (C4MIP now incorporated into CMIP5, for example, Table 2-3). SOM model development at these scales need to consider multiple model structures and variance in input data to reduce either

model-specific or data aggregation biases (Paustian et al., 1997), alongside comparisons between different modeling approaches to better understand the range of potential soil and ecosystem responses to climate change (Esser et al., 2011; Friedlingstein et al., 2006; Qian et al., 2010).

A number of ESM model comparisons, parameter validation, and benchmarking projects are ongoing (Table 2-3), with organizations like the World Climate Research Programme providing resources to promote project development. Researchers have repeatedly recognized that, for individual submodels or in its entirety, ESMs are fundamentally an interdisciplinary effort (Bonan et al., 2002; Pitman, 2003). Given the importance of climate change prediction across temporal and spatial scales, alongside the increasing sophistication in developing and evaluating climate change scenarios for mitigation and adaptive measures (Moss et al., 2010), we would like to emphasize the importance of this area of research and the need for collaboration between ESM researchers, SOM model developers, and SOM field and laboratory researchers alike to advance predictive accuracy through model-data integration. Expanding the network of scientists involved in either providing data for or advancing projects like the coupled model inter-comparison project (CMIP5) could lead to more rapid advances in understanding climate-soil interactions in the context of the global carbon cycle, in addition supporting to better predictions of future climate change.

2.4 Conclusions

We began this chapter by providing a brief background to SOM modeling, giving an overview of its history, philosophy, and foundational concepts. With this background we aimed to clarify the enduring value of the factors of soil formation as an overarching framework in SOM modeling. We also emphasized recent advances in SOM measurement methods and data-model integration, two areas with the potential to revolutionize the field in coming years.

We then highlighted recent advances in five areas of SOM model development: SOM stabilization mechanisms, saturation kinetics, temperature sensitivity, dynamics in deep soils, and

incorporation in earth system models. Across these five areas some challenges are universal, including in particular the integrating of understanding across varying scales. We support the view, suggested by others (Manzoni and Porporato, 2009; Stockmann et al., 2013), that SOM model use for hypothesis testing must be done with careful consideration of both the scale at which the model was developed, as well as the scope of the underlying questions being addressed. However, within these five areas some challenges are specific. SOM saturation kinetics, for example, are supported by both laboratory and field experimental data and additionally are relatively well understood from a SOM modeling standpoint. Yet it has seen extremely limited implementation in SOM models, due to its potential to drastically increase SOM model complexity while yielding SOM model improvements only in a narrow set of ecological conditions. Modeling SOM temperature sensitivity and deep soil dynamics, on the other hand, are more sharply limited by data availability, as temperature effects are difficult to isolate, while deep soils are difficult to access. In earth system modeling, however, the strongest limitations come from both the availability of sufficient computational technology to accommodate SOM models with higher complexity, as well as from varying data availability to drive SOM models for globally-scaled analyses. Understanding both the universal and the specific challenges in these areas of SOM model development can help target research to most effectively advance the field.

We see SOM research entering an exciting time. New measurement methods reveal new insights for the relationship between SOM's chemical nature, spatial distribution, and dynamics in the soil environment. Advances in computational capacity and development of collaborative networks for data sharing, management, and data-model integration increasingly relieve the bottlenecks in advancing the conceptual understanding of SOM. These efforts provide better environments to apply SOM models and test hypotheses for SOM dynamics across scales. As Pitman (2003) described more than a decade past (in regards to land surface modeling) the breadth of knowledge required to tackle comprehensive analysis using models of such complexity is vast, and the best approach is through multidisciplinary

collaborations. We recognize, alongside others (Stockmann et al., 2013), the continual importance of collaborative, interdisciplinary effort in SOM modeling.

Within this context there is also room for more openly sourced involvement in model-data integration. Data management is an increasingly sophisticated branch of research and development. Particularly if NSF funded, projects must generally make data management and the open provision of data a component of proposals and final products from research efforts. Libraries are developing capacity to house citable datasets, with standardized approaches to metadata and organizational structure. We believe data-model integration has only touched the surface of what is feasible, given more openly source collaborative networks of data sharing and model-data integration.

We urge the importance of considering scale in all of these developments, using general categories of microsite, site, regional, and global to frame the applicability of the SOM concepts being developed and tested. Due to overlapping levels of complexity, and the many ways in which data and models can interact, keeping consistency and clarity in underlying assumptions is particularly difficult. More standardized frameworks for data sharing and model-data integration will resolve this challenge. Given the continual and expanding importance of SOM models in understanding and managing soils as a natural resource we see this as a challenging, but fruitful, path forward.

Table 2-1 A selection of SOM reviews

Publication	Description
Oades, (1988)	“The retention of organic matter in soils” - clarifies terminology for soil C cycling and the linkage between the term ‘humus’ and ‘biomass’. Emphasis on physical stabilization and soil matrix interaction mechanisms that impact rates at which SOM is mineralized.
Sollins <i>et al.</i> , (1996)	“Stabilization and destabilization of soil organic matter: mechanisms and controls” - A conceptual framework for SOM dynamics aiming to bring together the state of the art in terms of mechanisms underlying SOM stability.
Falloon & Smith, (2000)	“Modeling refractory soil organic matter” - review of soil organic matter models- including static, dynamic, organismal- or process-based- approaches to modeling SOM with the longest turnover times.
Kuzyakov <i>et al.</i> , (2000)	“Review of mechanisms and quantification of priming effects”- consideration of SOM priming, and its potential to increase or slow SOM turnover rates. Additional: Fontaine <i>et al.</i> , (2007) – “Stability of organic carbon in deep soil layers controlled by fresh carbon supply”
Six <i>et al.</i> , (2002)	“Stabilization mechanisms of soil organic matter: Implications for C-saturation of soils” - evaluates mechanisms for SOM protection that have potential for saturation, proposing a fractionation method to evaluate soils for saturation kinetics.
Lützwow <i>et al.</i> , (2006)	“Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions – a review”- Methodical discussion of all SOM stabilization mechanisms occurring in temperate soils, identifying uncertainties and inconsistencies. Questions inherent chemical recalcitrance as a stabilization mechanism.
Trumbore, (2009)	“Radiocarbon and soil carbon dynamics”- A review of radiocarbon dating as an integrated measure of SOM cycling processes and turnover time over long-term timescales, centered on a state-factor approach to test hypotheses for SOM dynamics and showing differences in cycling dynamics across ecosystem components and timescales. Additional: Paul <i>et al.</i> , (1997)- “Radiocarbon dating for determination of soil organic matter pool sizes and dynamics”.
(Kleber, 2010)	“What is recalcitrant soil organic matter”- Complete examination of the term ‘recalcitrant’ in terms of general, mechanistic, and operational definitions. Examines logic for recalcitrance as a concept, arguing that it is largely semantic rather than providing meaningful connection to SOM dynamics.

Table 2-2 Comparison of a selection of SOM models simulating deep soil dynamics.

Model	Timestep, Simulation Timeframe	Depth	Drivers	SOM	DOM	Roots	Bioturbation
SOLVEG-II (Ota et al., 2013)	0.25hr timestep, immediate to long-term simulations	5.5m, 27 varying layer depths	Temp., moisture, soil texture	1 st order, CENTURY-type structure, 3 pools each layer (active, slow, passive)	<i>Explicit</i> , f(diffusion, advection, uptake, water flow, decomp)	Exponential function across depth	NA
C-TOOL (Taghizadeh-Toosi et al., 2014)	Monthly, medium to long-term simulations	100cm, 0 – 25cm & 25-100cm	Temp, clay content, soil C/N, OM inputs	1 st -order, 3 pool	<i>Implicit</i>	Exponential function across depth	NA
SOMPROF (Braakhekke et al., 2013)	Monthly, Medium to long-term simulations	0.7 – 2m, variable layer depths	Temp, moisture	1 st order, root & fragmented litter, leachable & non-leachable slow OM in mineral layer	<i>Implicit</i> , effective advection with liquid transport	1 st order decay	Single rate, with diffus. transport
RothPC-1 (Jenkinson and Coleman, 2008)	Monthly, Medium to long-term simulations	92cm: in 0-23, 23-46, 46-69, and 69-92cm depth increments	Temp, moisture, clay content	1 st order, including microbial biomass, humus, and inert OM pools	<i>Implicit</i>	1 st order decay, implicit in C flows through 'decomposable' versus 'resistant' plant OM pools	NA

Table 2-3 Selection of model intercomparison and model-data integration projects focused on carbon cycling and including a soils component.

Name	Description	Status and Resources	Select Contributions	Publications
International Land Model Benchmarking Project (ILAMB)	Model-data integration and intercomparison; develop and promote benchmarks; software system for benchmarking	Ongoing, www.ilamb.org	Identify ecosystem benchmarks for measured/modeled comparison, to reduce equifinality problem	(Luo et al., 2012)
Project for Intercomparison of Land surface Parameterization Schemes (PILPS)	Landsurface process modeling intercomparison of parameters; community-based documentation, comparison, and validation of parameters	Designed to be ongoing, listed as a former model intercomparison project by World Climate Research Programme, http://www.wcrp-climate.org/	Comparison of 1 st vs 2 nd generation models showed improvement when plant-soil interactions with atmosphere are dynamic, instead of passive; developing use of isotopes to improve parameterization	(Henderson-Sellers, 2006; Pitman, 2003)
Coupled Carbon Cycle Climate Model Intercomparison Project (C4MIP), now incorporated in the Coupled Model Intercomparison Project Phase 5 (CMIP5)	Isolate feedback between the carbon cycle and the climate in the presence of external forcing	Ongoing, http://c4mip.lsce.ipsl.fr/ , focus area within 5 th Coupled Modeling Intercomparison Project (CMIP5): e.g. http://journals.ametsoc.org/page/C4MIP	10 model comparison suggests high northern latitudes (poleward of 60degrees N) will be C sink to 2100, under warming and increased CO ₂	(Friedlingstein et al., 2006; Qian et al., 2010)

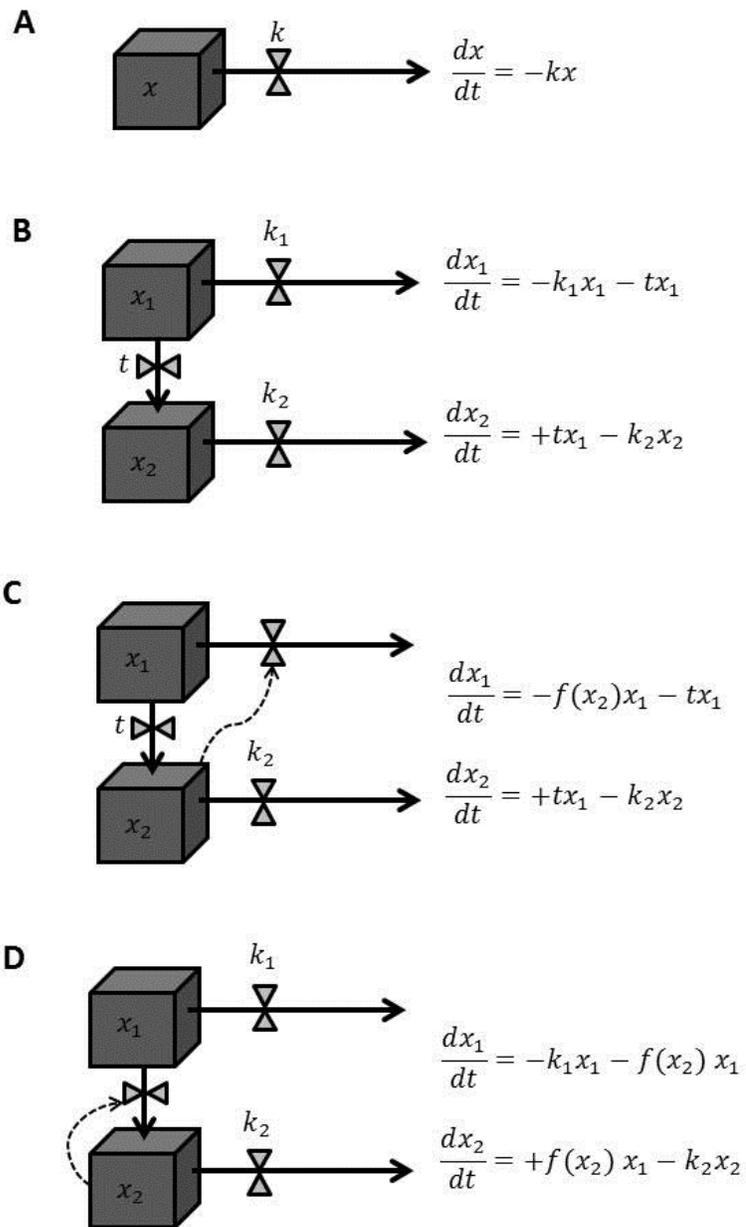


Figure 2-1 First order single and multi-compartment models (a & b, respectively) versus non-first order multi-compartment models showing compartment feedback on the rate of loss and compartment feedback on the rate of transfer between compartments (dotted arrow, c & d, respectively). Boxes indicate model states.

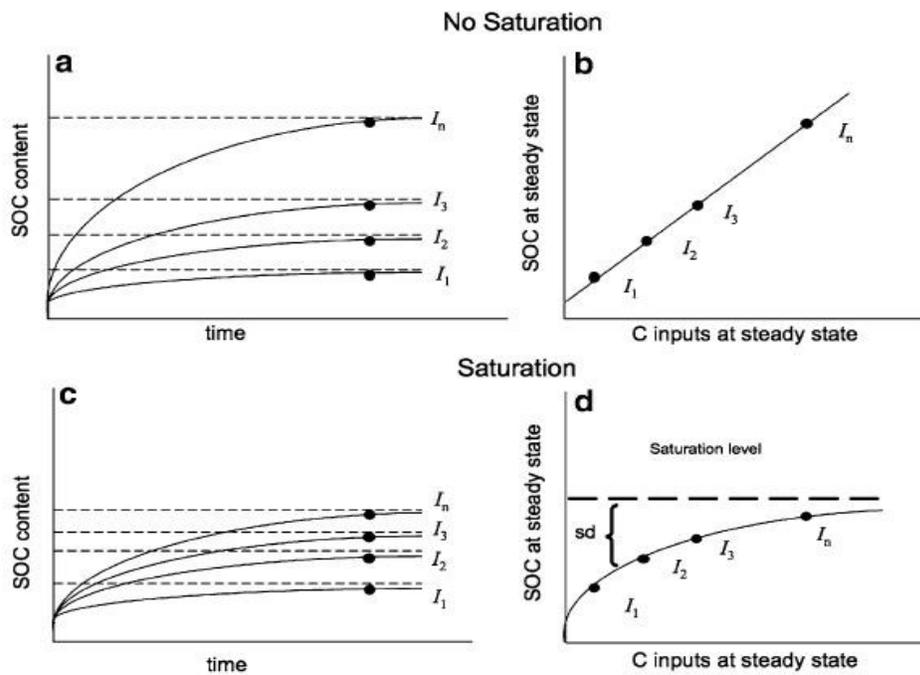


Figure 2-2 Theoretical relationship between C input level and soil organic C (SOC) contents at steady-state, with and without C saturation. Steady-state SOC accumulation dynamics expressed over time (a) produces a linear relationship when expressed over C input level (b) Under the conditions of C saturation, SOC stabilization with increasing input rates (at steady-state) is not proportional (c) resulting in an asymptotic relationship when expressed over C input level (d). Reprinted with permission from (Stewart et al., 2007).

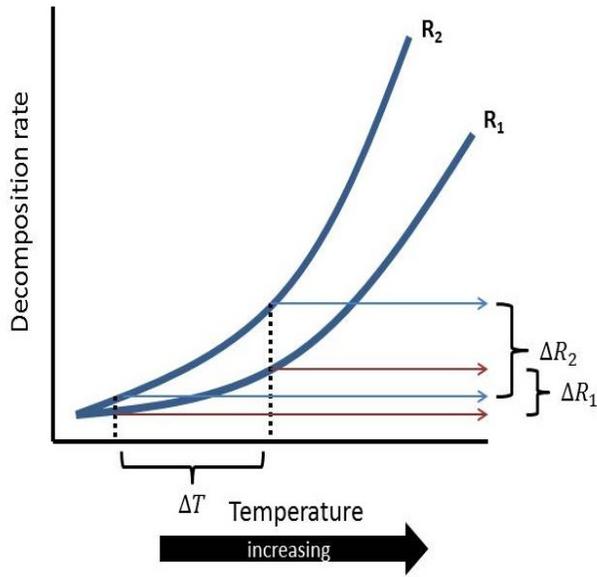


Figure 2-3 Hypothetical decomposition response curves with increasing temperature, showing greater temperature sensitivity of R_2 versus R_1 , as exemplified by ΔR_2 being larger in magnitude than ΔR_1 over the same temperature interval.

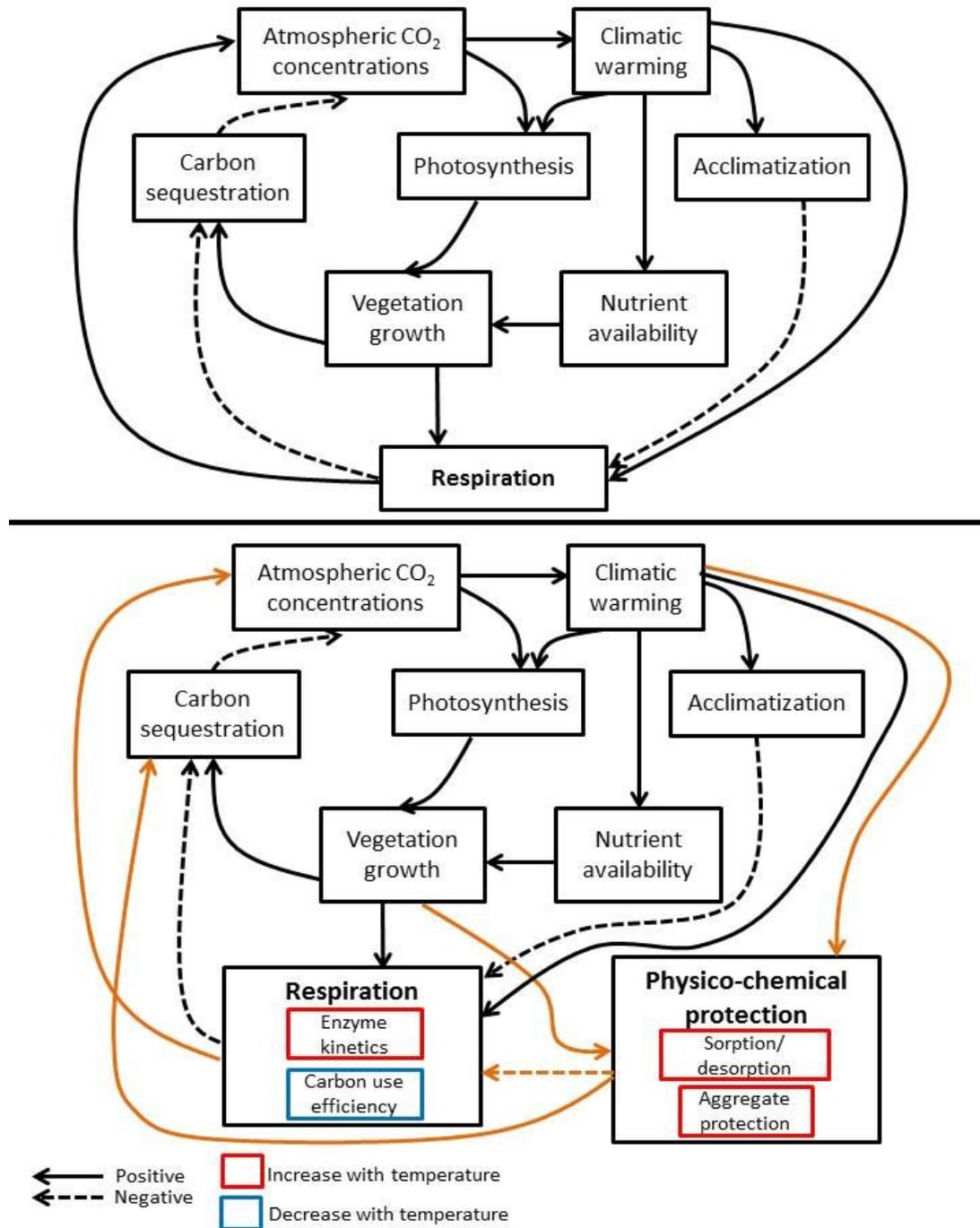


Figure 2-4 Conceptual diagram showing factors that can interact with atmospheric CO₂ emissions and soil respiration under climate warming, with hypothesized positive and negative feedbacks as originally described by Luo et al. (2001) (A), versus new approaches that separate mechanisms that affect microbial processes from mechanisms that affect SOM availability (B, vis à vis (Conant et al., 2011)). Colored boxes and lines can be considered a plausible scenario under increasing temperatures. Many other interactions are possible.

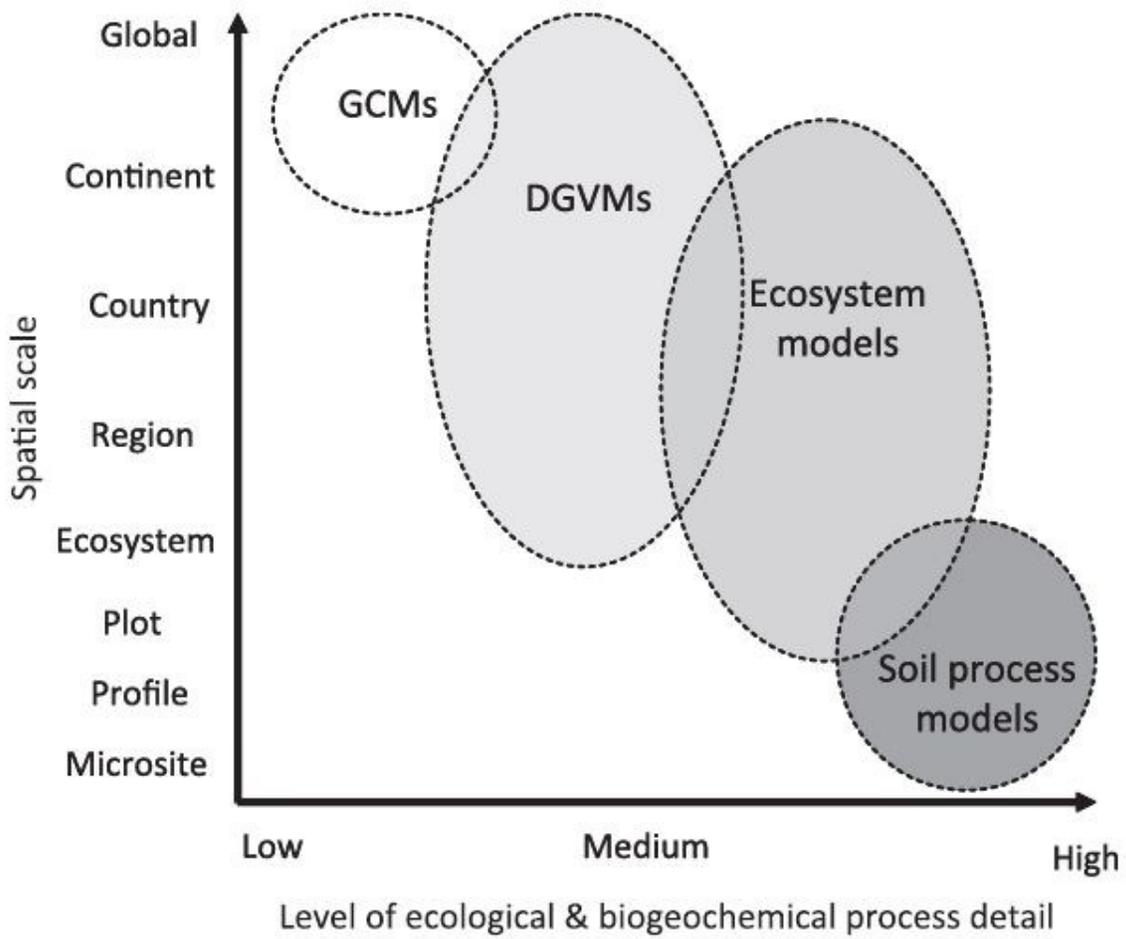


Figure 2-5 Conceptual grouping of carbon models across scales, in terms of process versus application, where GCMs refers to global circulation models (e.g. earth system models), and DGVMs refer to dynamic global vegetation models. Reprinted with permission from Ostle et al. (2009).

3 TRACKING THE FATE OF LITTER C INTO CO₂, MICROBIAL PRODUCTS AND DISSOLVED ORGANIC CARBON BY THE LITTER DECOMPOSITION AND LEACHING (LIDEL) MODEL USING A HIERARCHICAL BAYESIAN APPROACH TO ESTIMATE PARAMETERS AND VARIABILITY²

3.1 Introduction

Litter decomposition creates a dynamic link between atmosphere and terrestrial carbon C (Houghton, 2007), tying into concerns with the interaction of these two main global C pools in the context of global climate change (Friedlingstein et al., 2006, 2001). Decomposers interact dynamically with the physical characteristics and chemistry of litter, as well as with other biotic and abiotic factors (e.g. climate) through time. These interactions result in different rates of litter decomposition that have the potential to generate different types and quantities of decomposition products (e.g. Don and Kalbitz, 2005). Litter decomposition is therefore a fundamental mechanism determining the rate and partitioning of litter C—i.e. atmospheric CO₂ fixed via photosynthesis in terrestrial primary productivity—between returning to the atmosphere quickly as respired CO₂ and remaining in soils as partially decomposed litter or microbially-processed OM. Accurately representing litter decomposition in ecosystem and global C cycle models is therefore necessary to project climate change impacts, both to anticipate specific ecosystem changes as well as predict the magnitude and direction of feedbacks that affect global C dynamics.

Litter decomposition occurs through three general processes: fragmentation, catabolism to CO₂, and leaching (Swift et al., 1979). Current litter decomposition models are generally based on litter mass loss and CO₂ flux (e.g. Adair et al., 2008; Manzoni et al., 2012), an approach which does not consider leaching and the generation of dissolved organic matter (DOM). Dissolved organic matter can make up 6-39% of litter decomposition products (Don and Kalbitz, 2005; Magill and Aber, 2000; Qualls et al.,

² In preparation for *Soil Biology and Biochemistry* with W.B. Parton, J.L. Soong, N.T. Hobbs, M.F. Cotrufo, and K. Paustian.

1991). It is also recognized as an important near-term mechanism for vertical OM movement through soils, with the potential to contribute towards long-term SOM persistence by adsorption to soil minerals (Kaiser and Kalbitz, 2012). While some models simulate DOM movement in soils (Braakhekke et al., 2013; Jenkinson and Coleman, 2008; Ota et al., 2013; Tipping et al., 2012), there has been limited attention to the dynamics of DOM generation during litter decomposition. Studies show DOM generation can vary in quantity and chemistry between litter types and through time, in patterns that are often unrelated to cumulative litter mass loss dynamics (Don and Kalbitz, 2005; Soong et al., 2015). A dynamic model for DOM generation from litter decomposition is needed to examine the implications of these patterns on OM cycling, either at a fine scale—e.g. within a specific soil profile—or more generally in global biogeocycling processes.

Microbial carbon use efficiency (CUE)—the quantity of microbial biomass generated per unit of substrate use (Lekkerkerk et al., 1990)—is another important mechanism in litter decomposition, specifically within the process of catabolism to CO₂. Microbial CUE determines the partitioning of litter C between respired CO₂ versus the formation of microbial biomass and products. Microbial CUE is related to DOM generation and movement, as DOM shows increasing evidence of microbial processing across the vertical soil profile (Kaiser and Kalbitz, 2012; Tipping et al., 2012). However, to our knowledge this interaction has not been examined in a litter decomposition model.

Evidence suggests microbial CUE is often variable during litter decomposition, depending on the decomposition environment, chemical characteristics of substrates being decomposed, and the physiological characteristics of microbes and microbial communities (Frey et al., 2013; Lekkerkerk et al., 1990; Manzoni et al., 2008). However many widely used models simulate CUE as a static variable (e.g. DAYCENT (Parton, 1988)). This is an important area for litter decomposition model development, as evidence supports microbial products as an important contributor to SOM formation (Miltner et al., 2011; Schmidt et al., 2011). Theoretical implications of variable CUE in SOM formation are summarized

in the Microbial Efficiency-Matrix Stabilization (MEMS) framework, proposing potential for greater persistence of litter OM that is more efficiently decomposed due to greater generation of microbial material that can then be stabilized in the soil matrix (Cotrufo et al., 2013). The MEMS hypothesis is suggested as an alternative to past hypotheses linking SOM stability to inherent litter chemical recalcitrance, that have since been strongly criticized (Dungait et al., 2012; Kleber, 2010; Kleber et al., 2011). Litter decomposition models that include variable CUE would more accurately reflect partitioning of decomposed litter C to CO₂ *versus* microbial materials, and thus be able to test new hypotheses linking microbial processes to SOM persistence (Wieder et al., 2014).

In this paper we propose the Litter Decomposition and Leaching (LIDEL) model as a new approach to modeling litter decomposition that 1) includes explicit modeling of DOM as a litter decomposition product, and 2) dynamically links substrate chemistry with variable CUE and the generation of DOM and other litter decomposition products. In the LIDEL model, we focus on the control of CUE by litter N and lignin content. Nitrogen, whether internally (e.g. as a component of plant litter) or externally (e.g. as present in the surrounding environment) available, is an important driver of litter decomposition dynamics (Adair et al., 2008; Aerts, 1997; Manzoni et al., 2008; Sinsabaugh et al., 2013). Lignin is a litter chemistry metric that also shows strong explanatory power when incorporated into litter decomposition models (Adair et al., 2008), and has been linked to mechanistic controls on microbial processes during decomposition (Moorhead et al., 2013). The LIDEL model specifically integrates Moorhead et al. (2013) and Sinsabaugh et al. (2013) hypotheses for lignin and N impacts on microbial CUE, with experimental data from Soong et al. (2015) for the impact of litter chemistry on the generation of CO₂ *versus* DOC from litter decomposition.

Linking changes in measured C pools with conceptual understanding of decomposition dynamics, particularly as C moves from the surface into the soil matrix, is a fundamental challenge modeling litter decomposition and soil C dynamics (Elliott et al., 1996). There are a variety of established

methods to optimize model parameters and evaluate uncertainty in model performance in state-space models characteristic of modeling C dynamics (e.g. Del Grosso et al., 2010; Ogle et al., 2010, 2007). However, these analyses are often not satisfactory in accounting for multiple types of measurement data, accommodating different types of measurement and model uncertainty, or integrating these two components in time-series models and observations. Hierarchical Bayesian methods offer an approach to factor highly complex problems with high dimensionality into problems with lower dimensions, specifically by separating the problem into the process model (e.g. the LIDEL model), data models, and associated parameter models, and having uncertainty associated with each component (Berliner, 1996; Clark, 2007; Geremia et al., 2014). Bayesian methods for model-data integration provides a powerful approach to estimate unknown model parameters and compare C cycling models (Tuomi et al., 2008), clarifying how measured data connect to ecological hypotheses (Hararuk and Luo, 2014). Bayesian methods can also help identify areas where data are needed or where additional data would help clarify the understanding of underlying dynamics (Braakhekke et al., 2013). Hierarchical Bayesian methods have further been used to successfully partition variability in C cycling dynamics (Ogle and Pendall, 2015). In the hierarchical Bayesian framework it is also possible to separate model error from observation error if we use informative priors on error terms, for example if error in a specific measurement technique is well understood (Hobbs and Hooten, in press).

In this paper we present the LIDEL model structure and assumptions, as well as parameter estimates using hierarchical Bayesian methods (Berliner, 1996; Clark, 2007; Geremia et al., 2014) to integrate LIDEL model simulations with data from an experiment measuring the generation of decomposition products from five litters that varied in initial lignin and N content (Soong et al., 2015). We explore separate hypotheses for N control on litter decomposition and the efficiency of DOC generation from litter fractions. Specifically we examine 1) a logistic *versus* a linear relationship between N content, N controls on litter decomposition rates, and microbial CUE, to test whether N limitation is

better modeled as occurring suddenly at a threshold, or as occurring more gradually as N content decreases. We also examine 2) equal DOC/CO₂ generation efficiency from both the soluble and cellulose-dominated litter fractions *versus* higher DOC generation from the soluble litter fraction. The combination of these alternate hypotheses for 1) N limitation and 2) DOC/CO₂ generation efficiency yielded four separate LIDEL model formulations. Parameter estimates and overall model predictive accuracy were compared between these four LIDEL model formulations, to identify the model structure that best predicted measured litter decomposition dynamics.

3.2 Material and methods

3.2.1 LIDEL model description

In the LIDEL model (Figure 3-1) we propose separating litter into three C fractions including: water soluble, lignin, and non-lignin structural (NLS). A similar fractionation approach separating plant litter into lignin, labile, and cellulose pools has been successfully applied in other models to include the impacts of microbial growth efficiency on C dynamics, yielding improved global simulations of soil C (Wieder et al., 2013). However we use water soluble litter instead of labile litter to better link to DOC and the ecological importance of water in generating and moving this OC fraction. We model lignin, similarly to Weider et al. (2013), in order to explicitly implement the Moorhead et al. (2013) hypotheses for lignin control on CUE, described below. The remaining litter material is estimated by difference and thus termed non-lignin structural. However we assume that the NLS fraction is dominated by cellulose and hemicellulose—termed holocellulose—and treat it as such when implementing Moorhead et al. (2013) hypotheses for lignin controls on decomposition. We therefore refer to the NLS pool using the more familiar term holocellulose, even though technically by our definition this pool will contain a small quantity of non-holocellulose material.

In order to incorporate dynamic microbial CUE impacts on the generation of microbial biomass and microbial products we model litter material movement into microbial biomass and then microbial

products pools, with losses to DOC and CO₂. It should be noted that lignin does not directly contribute to microbial biomass, but only decomposes to CO₂ and DOC. This is drawn from the Moorhead et al. (2013) hypothesis that lignin is not energetically favorable for microbes to decompose, and is therefore decomposed to access holocellulose without yielding microbial biomass directly (Moorhead et al., 2013). It should also be noted that microbial products only contains structural microbial material, as soluble microbial products from microbial biomass will be lost as DOC (Figure 3-1).

The mathematical representation of Figure 3-1 is expressed as a system of seven ordinary differential equations, where:

$$\frac{DC_1}{dt} = -\mu_k k_1 C_1 , \quad \text{Eqn 1}$$

$$\frac{DC_2}{dt} = -\mu_k k_2 C_2 , \quad \text{Eqn 2}$$

$$\frac{DC_3}{dt} = -k_3 C_3 , \quad \text{Eqn 3}$$

$$\frac{DC_4}{dt} = -k_4 C_4 + \mu_\beta \beta_2 (1 - \lambda_1) \mu_k k_2 C_2 + \mu_\beta \beta_1 (1 - \lambda_4) \mu_k k_1 C_1 , \quad \text{Eqn 4}$$

$$\frac{DC_5}{dt} = -k_5 C_5 + \beta_3 (1 - \lambda_2) k_4 C_4 , \quad \text{Eqn 5}$$

$$\frac{DC_6}{dt} = \lambda_1 \mu_k k_2 C_2 + \lambda_3 k_3 C_3 + \lambda_2 k_4 C_4 + \lambda_3 k_5 C_5 + \lambda_4 \mu_k k_1 C_1 , \text{ and} \quad \text{Eqn 6}$$

$$\begin{aligned} \frac{DC_7}{dt} = & \left((1 - \mu_\beta \beta_1) (1 - \lambda_4) \right) \mu_k k_1 C_1 + \left((1 - \mu_\beta \beta_2) (1 - \lambda_1) \right) \mu_k k_2 C_2 + (1 - \lambda_3) k_3 C_3 + \\ & \left((1 - \beta_3) (1 - \lambda_2) \right) k_4 C_4 + (1 - \lambda_3) k_5 C_5 . \end{aligned} \quad \text{Eqn 7}$$

The LIDEL model runs on a daily time step. Parameters k_1 and k_2 are the maximum rates (day⁻¹) of water soluble and holocellulose decay, and are parameters fitted in our analysis. The rate (day⁻¹) of microbe biomass decay (k_4), the generation of microbial products from microbe biomass (β_3), and the generation of DOC from the decay of microbe biomass (λ_2) are also fitted parameters in our analysis. Parameters β_1 and β_2 are the maximum growth efficiencies (g microbial biomass/g decayed material) for microbial use of water soluble and holocellulose litter, set at values of 0.6 and 0.5, assuming the maximum CUE stipulated by Sinsabaugh et al. (2013) for soluble C and assuming a lower maximum for

decomposition of holocellulose (Figure 3-2b). The remaining parameters are based on hypotheses described in the following sections.

3.2.1.1 Linking hypotheses for microbial CUE and litter decay

We differentiate individual N and lignin effects in the LIDEL model by setting a maximum CUE limit and a threshold for N effects on CUE (Moorhead et al., 2013; Sinsabaugh et al., 2013). Lignin affects litter decomposition, as well as microbial CUE, by limiting microbial access to usable plant material (i.e. holocellulose) (Herman et al., 2008; Manzoni et al., 2008; Moorhead et al., 2013; Sinsabaugh et al., 2013). We adapted these hypotheses to set lignin and N limitations on decomposition and CUE in the LIDEL model, as based on the initial litter N content and the dynamic lignocellulose index (L_c), calculated as;

$$L_c = \frac{\text{lignin } (C_3)}{\text{lignin } (C_3) + \text{NLS } (C_2)}. \quad \text{Eqn 8}$$

Based on prior publications (Moorhead et al., 2013; Sinsabaugh et al., 2013) and DOC generation dynamics in the Soong et al (2015) experiment we hypothesized that the water soluble and holocellulose pools are affected by both L_c and N. We assumed the litter chemistry (i.e. either L_c or N) exerting the greatest limitation at any given point in time during decomposition is, at that time point, controlling decomposition dynamics and microbial uptake of these pools. Therefore;

$$\mu_k = \text{minimum}(\gamma, \varepsilon_k), \text{ and} \quad \text{Eqn 9}$$

$$\mu_\beta = \text{minimum}(\gamma, \varepsilon_\beta), \quad \text{Eqn 10}$$

where μ_k is the litter chemistry limitation on the maximum rate of decay for the water soluble and holocellulose fractions, μ_β is the litter chemistry limitation on the maximum rate of microbial uptake of these pools. The value for μ_k is determined by the minimum of γ — the rate modifier based on N limitation (Figure 3-3)—*versus* ε_k , a rate modifier for L_c -dependent limitation on decay. The value for μ_β is determined by the minimum of γ *versus* ε_β , a rate modifier for L_c -dependent limitation on CUE (Figure

3-2). Moorhead et al. (2013) propose microbes do not decompose lignin when $L_c < 0.4$, when holocellulose is highly available for microbial use. They further propose a linear increase in rates of lignin decay accompanied by a linear decrease in rates of holocellulose decay when L_c is between 0.4 – 0.7. Finally, they propose an equal decay rate of both pools when $L_c > 0.7$. We approximated these equations with a continuous equivalent (Figure 3-2). We expressed ε_k as;

$$\varepsilon_k = e^{-3.0 * L_c}. \quad \text{Eqn 11}$$

We expressed the control of L_c on water soluble and holocellulose CUE (ε_β) when L_c is less than 0.7 as:

$$\varepsilon_\beta = 1 - e^{-0.7(|L_c - 0.7| * 10)}. \quad \text{Eqn 12}$$

We expressed the control of L_c on the rate of lignin decay (k_3 , in units of day^{-1}), based on the holocellulose maximum rate of decay (k_2 , in units of day^{-1}), as:

$$k_3 = k_2 \frac{0.2}{(1 + \frac{200}{e^{8.15 L_c}})}. \quad \text{Eqn 13}$$

Microbial products are hypothesized to be an important contributor to SOM formation (Cotrufo et al., 2013), but are difficult to measure (Preston et al., 2009), and their dynamics remain poorly understood. We assume microbial products are decomposed slowly, and do not directly contribute to the generation of microbial biomass (Figure 3-1). We expressed the rate of microbial products decay (k_5 , in units of day^{-1}), for simplicity (i.e. without adding additional model parameters), as similar to the maximum possible rate of lignin decay, where:

$$k_5 = k_2 e^{-2.1}. \quad \text{Eqn 14}$$

Sinsabaugh et al. (2013) link substrate N content to microbial CUE, providing evidence for a threshold for N availability above which N does not limit CUE. Based on this hypothesis, we propose that above 3% N, either in litter or as available to microbes from external sources (e.g. soil, which we did not consider in this analysis), CUE and litter decomposition are unaffected by N availability. However, below that threshold we explore two mathematical expressions of N limitation:

$$\gamma_1 = \frac{1}{1+e^{-N_{Max}(\tau-N_{mid})}} \phi, \text{ and} \quad \text{Eqn 15}$$

$$\gamma_2 = N_{min} + \frac{1-N_{min}}{N_{Max}} \phi, \quad \text{Eqn 16}$$

where γ modifies rates of decay from the water soluble and holocellulose C pools, as well as the rate of C uptake by microbes. In both Eq.15 and 16, N_{Max} is the maximum percent litter N for a N effect while ϕ is the internally available initial litter percent N. In Eq. 15, N_{mid} determines the midpoint of the N limitation curve. In Eq. 16, N_{min} is the intercept determining minimum N limitation. N_{min} can be considered a measure of external N availability, and could be an estimated parameter with application of the LIDEL model in systems that vary by both litter N and externally available N (e.g. connecting the LIDEL model to a model of soil organic matter dynamics) (Figure 3-3).

3.2.1.2 Hypotheses from experimental data: DOC versus mass loss

Data from the litter decomposition experiment by Soong et al. (2015) were used to develop the remaining structure of the LIDEL model. In this experiment five litter types were selected that exhibited a range of initial % N and initial L_c (Table 3-1), in order to examine their relative impacts on the character and quantity of DOC and CO_2 generation across a 365 day incubation. Each litter type was exposed to a microbial inoculum and allowed to decompose in absence of soil and without any additional N, with periodic leaching events that were more frequent in early stages of decomposition (approximately every 1-3 days, then approximately weekly, then approximately every 1-2 months). Measurements of DOC and CO_2 were taken at each leaching event, and measures of litter mass loss were taken by destructive harvesting half of the samples at day 95 and the remaining half at the conclusion of the experiment on day 365 (for more details about the experiment see Soong et al.,2015). This experiment provides a unique dataset explicitly evaluating the fractionation of DOC generation *versus* CO_2 through time, across litters that vary in their N and L_c chemistry. We use these data to develop empirically-based hypotheses for the generation of DOC from decomposition from the litter pools included in the LIDEL model.

We hypothesized linear declining relationships between the ratio of DOC *versus* litter mass loss (i.e. $\text{DOC}/(\text{DOC}+\text{CO}_2)$) as a function of initial litter % N and L_c , with highest proportion of DOC generation at the lowest initial % N and L_c values. Based on these hypotheses, we examined the predictive power of initial litter % N and L_c in estimating DOC generation, across the range of DOC *versus* litter mass loss observed in the Soong et al. (2015) experiment (0.15 – 0.48 g DOC per g litter mass loss from day 10 - 20, 0.004 – 0.27 g DOC per g litter mass loss from day 20 - 365). We examined the predictive power of these relationships individually as well as by taking the minimum of the DOC *versus* mass loss predicted by each factor—similar to the approach applied to determine μ_k and μ_β (Eqn's 8 and 9). Predictions using the minimum of the two factors had a higher r^2 than predictions based on either of these factors individually (minimum predicted: $r^2=0.319$, slope=0.616, intercept=0.113; L_c predicted: $r^2=0.149$, slope=0.477, intercept=0.111; N predicted: $r^2=0.105$, slope=0.269, intercept=0.128), suggesting litter N and L_c influence different mechanisms for DOC generation during decomposition. Predictions had a substantially higher r^2 as well as a slope closer to 1 and intercept closer to 0 when accounting for the higher proportion of DOC generation between early *versus* later decomposition (i.e. day 10 – 20 *versus* day 20 – 365), again using the minimum of predictions from initial litter %N and L_c (Figure 3-4) (minimum predicted: $r^2=0.862$, slope=0.991, intercept=0.018; L_c predicted: $r^2=0.704$, slope=0.896, intercept=0.01; N predicted: $r^2=0.613$, slope=0.702, intercept=0.012). The generation of DOC has been linked to the water soluble fraction of litter (Magill and Aber, 2000; Smolander and Kitunen, 2002). This is further supported by Soong et al. (2015) data that show early DOC generation is strongly plant-derived, and strongly predicted by the hot water extractable fraction. We therefore assume that early DOC generation is predominantly derived from the litter water soluble fraction, and hypothesize that DOC generated from both the water soluble and holocellulose litter fractions are similarly affected by litter N and L_c . We express the rate of DOC generation from decomposition of water soluble and holocellulose C (λ_4 and λ_1) as;

$$\lambda_4 = \text{minimum} \left(\left(E_{SM_{max}} - \frac{(E_{SM_{max}} - E_{SM_{min}})}{L_{cMax}} * L_c \right), \left(E_{SM_{max}} - \frac{(E_{SM_{max}} - E_{SM_{min}})}{N_{Max}} * \phi \right) \right), \text{ and} \quad \text{Eqn 17}$$

$$\lambda_1 = \text{minimum} \left(\left(E_{HM_{max}} - \frac{(E_{HM_{max}} - E_{HM_{min}})}{L_{cMax}} * L_c \right), \left(E_{HM_{max}} - \frac{(E_{HM_{max}} - E_{HM_{min1}})}{N_{Max}} * \phi \right) \right). \quad \text{Eqn 18}$$

where $E_{SM_{min}}$ and $E_{SM_{max}}$ are the minimum and maximum leached fractions from the soluble pool, $E_{HM_{min}}$ and $E_{HM_{max}}$ are the minimum and maximum leached fraction from the holocellulose pool, and L_{cMax} is the maximum L_c index. We use this component of the LIDEL model to evaluate our hypotheses for DOC generation efficiency from litter decomposition, developing two formulations of the LIDEL model with respect to the maximum and minimum leached fractions from the soluble versus the holocellulose pools. In one formulation these values were set equal to each other, at a minimum and maximum of 0.005 day^{-1} and 0.15 day^{-1} . In the other formulation the soluble pool values were set higher than the holocellulose pool values, at 0.1 and 0.5 day^{-1} versus 0.001 and 0.1 day^{-1} . The latter approach assumes greater efficiency of plant-derived DOC release from decomposition of the holocellulose pool versus the soluble pool.

Finally, in the LIDEL model DOC is also generated from lignin, microbes, and microbial products. The generation of soluble microbial products from microbial biomass turnover is not well understood and is therefore a fitted parameter in this analysis. We assume for the lignin and microbial products pools that only a very small, constant portion of DOC is generated from decomposition. We used measurements of DOC generation from late in alfalfa decomposition (that decomposed very quickly and had very little mass at the end of the incubation) to set this rate, where:

$$\lambda_3 = 0.038 \text{ g DOC/g decayed material} \quad \text{Eqn 19}$$

3.2.1.3 LIDEL initial conditions

The initial conditions of the LIDEL model pools (referred to by τ subscripts) were assumed to be determined by the fraction of initial litter material in the soluble, lignin, and DOC pools, with the remaining material in the holocellulose pool. These initial conditions were calculated as;

$$C_{1\tau i} = (C_{Ti} f_{s_i}) - (C_{Ti} f_{s_i} f_{DOC}), \quad \text{Eqn 20}$$

$$C_{2\tau i} = C_{Ti} - (C_{Ti}(f_{s_i} + f_{LIG_i})), \quad \text{Eqn 21}$$

$$C_{3\tau i} = C_{Ti} f_{LIG_i}, \quad \text{Eqn 22}$$

$$C_{4\tau i} = 0, \quad \text{Eqn 23}$$

$$C_{5\tau i} = 0, \quad \text{Eqn 24}$$

$$C_{6\tau i} = C_{Ti} f_{s_i} f_{DOC}, \text{ and} \quad \text{Eqn 25}$$

$$C_{7\tau i} = 0, \quad \text{Eqn 26}$$

where C_{Ti} is the total initial litter C mass of litter i , f_{s_i} is the soluble fraction for a given litter i , f_{DOC} is the fraction of soluble material that is not microbially processed, and f_{LIG_i} is the lignin fraction for a given litter i .

3.2.2 Statistical Approach

3.2.2.1 Data

Data used in this analysis include experimental time series data from the laboratory litter decomposition experiment described in detail in Soong et al. (2015) and literature data (Adair et al., 2008; Parton et al., 2007) for the initial litter chemistry of the five litters; alfalfa (*Medicago sativa*), ash (*Fraxinus excelsior*), big bluestem (*Andropogon gerardii*), oak (*Quercus macrocarpa*) and pine (*Pinus ponderosa*). To initialize the LIDEL model C pools we used Soong et al. (2015) experimental data for measurements of initial litter chemical fractions. The acid unhydrolyzable residue (AUR) measured from the acid detergent fiber (ADF) digestion method (Van Soest and Wine, 1968) used in Soong et al. (2015) is a reasonable approximation of lignin at the initial phase of the experiment when the litters have not been exposed to microbial processing. It therefore was the only source of data used to inform the initial size of the lignin C pool in the LIDEL model. However the connection is less clear between the soluble C

pool used in the LIDEL model and either hot water extraction (noted as HWE) or measurement of this fraction as the mass loss during NDF digestion (Soong et al., 2015). Therefore we used both of these measurements from Soong et al. (2015), supplemented with literature values across the five litters to more accurately reflect their variance. Conceptually, the initial value of the DOC pool in the LIDEL model is representative of soluble litter C that is released immediately with exposure to water, without any interaction with microbial processes. We made the assumption that the DOC released in the first 10 days of the experiment is an approximation of this initial DOC value. The initial holocellulose pool was assumed to consist of the remaining initial litter C after removal of the soluble, initial DOC, and lignin litter C (Eq. 21). Full details on these data and their use to initialize the LIDEL model are described in Appendix 1.

We additionally used the series of CO₂, DOC, and total mass loss measurements taken by Soong et al. (2015) through the 365 day incubation to evaluate LIDEL temporal dynamics. Each time series measurement had three replicates for each litter. Full details on these data and their use to evaluate the LIDEL model are described in Appendix 2.

3.2.2.2 Hierarchical Bayesian Analyses

Using the data described above, we applied hierarchical Bayesian models to use the experimental data to estimate initial LIDEL model pools as well as five parameters that drive LIDEL temporal dynamics. The five parameters include the decay of the soluble (k_1), non-lignin structural (k_2), and microbial biomass pools (k_4), the generation of microbial products from microbe biomass (β_3), and the generation of DOC from the decay of microbe biomass (λ_2). These parameters are important for the dynamics of litter decomposition through time as well as the generation of products from microbial processes. However, they are poorly understood in part due to the difficulty in measuring them experimentally.

The LIDEL model includes several equations where the minimum of two values drive model dynamics at a given point in time (Eq.'s 9, 10, 17, and 18). The LIDEL model is therefore non-linear and cannot be solved analytically, requiring the use of an ordinary differential equations solver to resolve model dynamics into daily time steps. We split the data and processes into two hierarchical Bayesian analyses. The first analysis estimated the initial conditions (IC) of the LIDEL model. The second analysis used the results of the first as priors in the estimate of LIDEL temporal dynamics (TD), using the four LIDEL formulations under consideration (linear *versus* logistic N control, Eqns 15 vs 16, and equal *versus* unequal DOC generation efficiency from the soluble and holocellulose pools, Eqns 17 & 18). This approach was meant to reduce the number of estimated parameters in the TD analysis, where the ordinary differential equations solver is required. The TD analysis used the posterior distributions of the IC analysis as priors to initialize LIDEL model pools on day 0. To further simplify the TD analysis a subset of measured time points for DOC and CO₂ were used to estimate a subset of latent states, measurement error and model error.

Since the five main parameters of interest for the TD analysis each have a single value across all litter types and all time points, subsetting time points was considered an appropriate method to reduce computational complexity by reducing the number of estimated values (by reducing the estimated latent states) while still informing the parameters of interest with time series measurements across the decomposition experiment. The subset of time points were selective to be representative of the 'early', 'middle' and 'late' stage decomposition dynamics identified by Soong et al. (2015). The subset of time points included all measurements for all litter types on days 7, 15, 28, 64, 95, and 365. The remaining measurements were used for a non-exhaustive cross validation at each iteration of the MCMC, calculating the root mean square error (RMSE) for the model prediction of all measured time points excluded from the subset. Litter mass remaining measurements were only taken at two time points, on day 95 and day 365. Therefore all mass measurements were used in the TD analysis to estimate model

parameters. RMSE results are therefore an indication of model fit for predicting out-of-sample DOC and CO₂ measurements.

In both the IC and the TD hierarchical Bayesian analyses, latent states and parameter marginal posterior distributions were estimated using a random-walk Metropolis Hastings Markov Chain Monte Carlo (MCMC) algorithm. The analyses were written in R (R Core Team, 2014). We used the *Isoda* function in the R package *deSolve* as the ODE solver (Soetaert et al., 2010). Three MCMC chains were run out 100,000 iterations for the IC analysis, discarding the first 50,000 iterations as the burn-in period. In the four LIDEL model formulations considered in the TD analysis, 80,000 iterations were simulated total with the first 40,000 iterations discarded as the burn-in period. Individual chains were assessed visually for convergence using trace and marginal density plots, as well as using Geweke convergence diagnosis Z-scores (Geweke, 1992). The 3 chains were then assessed for convergence using the Gelman-Rubin MCMC convergence diagnostic (Gelman and Rubin, 1992). Once the 3 chains passed convergence tests, summary statistics of model parameters were evaluated (mean and 95% Bayesian credible intervals). All of these convergence diagnoses and summary analyses were completed using the *coda* package in R (Plummer et al., 2006). Details for both the IC and the TD analyses, including the full Bayesian models as well as MCMC algorithms are described in Appendix 1 and 2, respectively.

3.3 Results

Summary statistics for estimates of litter fractions—including the soluble and lignin fractions by litter type as well as the initial DOC fraction—are presented in Table 3-2. Parameter estimates for the variance of the hot water extraction and mass-difference soluble fraction measurements, as well as the final estimated soluble fraction parameters are presented in Figure 3-5. Across litter types, the initial lignin fraction in the LIDEL model—informed by AUR data in the Soong et al. (2015) experiment—shows a narrower width than the other fractions estimated in this analysis (Table 3-2).

The hierarchical Bayesian approach allows litter fractionation parameter variance and uncertainty, estimated in the IC analysis, to be carried into the estimates of LIDEL temporal dynamic parameters. Overall there is high variability in LIDEL estimates (Figure 3-6). This is particularly apparent in LIDEL DOC and CO₂ predictions, as indicated by the width of 95% BCI's (Figure 3-6). These wide ranges are likely related to the variable initial litter fraction estimates yielded from the IC analysis, used to initialize the LIDEL model litter pools. Both the initial soluble and DOC pools are less constrained by data than the initial lignin pool. However in the TD analysis the data suggest the soluble LIDEL pool decomposes much more quickly than the holocellulose pool and is therefore responsible for providing the input that drive DOC and CO₂ generation, particularly early in decomposition (Table 3-3). Variability in the initial soluble pool size for each litter will therefore contribute to variability in model estimates of DOC and CO₂ generation.

Models 1, 2 and 3 had comparable k_1 estimates, although the last was less well informed by the data (as shown by its broader 95% BCI width, Table 3-3). Estimates of k_2 were more tightly constrained, only ranging by 0.0045 day⁻¹ between all LIDEL model formulations. Microbial biomass turnover was weakly informed by the data but suggests fast turnover, with all estimated means exceeding 0.5 and with values that were closer to the upper range of the 95% BCI than the lower range (indicating a predominance of higher parameter values in the MCMC). Microbial product generation from microbial biomass turnover was very weakly informed by the data in models 1, 2, and 4, and not informed by the data in model 3. DOC from microbial biomass was more strongly informed by the data, showing similar characteristics in models 1 & 2 (higher) versus models 3 & 4 (lower). According to RMSE values the lowest predictive accuracy for out-of-sample DOC and CO₂ measurements was model 4, versus the highest predictive accuracy in models 1 and 3 (Table 3-3). The measured/modeled comparison of estimated time points, however, shows improved mass remaining estimation in models 1 & 2 versus 3 & 4 (Figure 3-6, A & D versus G & J), and improved high DOC predictions in models 2 & 4 versus models 1 &

3 (Figure 3-6, E & K versus B & H). It is important to note that all mass measurements from Soong et al. (2015) were used in the TD Bayesian analysis. We only used out-of-sample measurements to calculate RMSE values, which therefore only assesses out-of-sample measured vs. model prediction for DOC and CO₂. The RMSE values therefore do not factor in the bias in LIDEL mass remaining prediction apparent in Model 3 and 4 results (Figure 3-6, G & J). It is also notable that RMSE is lower with models 1 and 3 versus 2 and 4, whereas in the latter there is a clear improvement in model predictions of high DOC measurements (Figure 3-6, E & K versus B & H). However DOC predictions also become more variable in models 2 and 4, as indicated by the wider 95% BCI's (Figure 3-6).

3.4 Discussion

An ongoing debate in modeling terrestrial OM dynamics is the degree to which explicit modeling of microbial biomass and processes is needed to accurately simulate C cycling and ecosystem dynamics (Stockmann et al., 2013; Treseder et al., 2012). This debate is in part centered on accurately capturing ecosystem responses to direct and indirect human impacts, such as global warming and land use change (Wieder et al., 2014). New modeling efforts are aimed to better reflect microbial processes in litter decomposition and SOM dynamics (Davidson et al., 2014; Moorhead and Sinsabaugh, 2006; Wieder et al., 2013; W. R. Wieder et al., 2014). However, there is the potential for increases in model complexity and unrealistic oscillatory behavior with the added feedback between explicit microbial biomass and decomposition dynamics (Wang et al., 2014). Data to drive and evaluate models with explicit microbial biomass and mechanisms are also more limited (Treseder et al., 2012). With the LIDEL model, we look to strike a balance between model complexity and simulating dynamic microbial processes. The LIDEL model includes an explicit microbial biomass pool, is driven with broadly available data, and includes dynamic microbial CUE, but maintains a relatively simple first-order structure by not linking microbial biomass directly to decomposition rates (Figure 3-1).

The LIDEL model incorporates variable microbial CUE and litter chemistry to explicitly simulate DOC *versus* structural microbial products generation during litter decomposition, an important new direction for the simulation of litter decomposition dynamics in SOM models. DOC and persistent microbial products are recognized both as important contributors to SOM dynamics across soil profiles, and as shortfalls in many SOM models (Rumpel and Kögel-Knabner, 2010; Schmidt et al., 2011). From this analysis there remains uncertainty in the ‘internal’ dynamics of the LIDEL model, particularly pertaining to microbial biomass turnover and the fractionation between microbially-derived soluble versus structural material. However, the LIDEL model provides a robust theoretical structure to connect litter chemistry and microbial processes to the generation of these separate products (Moorhead et al., 2013; Sinsabaugh et al., 2013), as well as suggest testable hypotheses. For example, we only used data on total DOC and CO₂ to inform our parameter estimations. We did not inform our statistical models with data indicating the relative contribution of microbially-derived versus plant-derived DOC. Therefore while the DOC/CO₂ fractionation difference explored in models 1 and 3 versus 2 and 4 supported the hypothesis of higher efficiency in the generation of DOC/CO₂ from soluble litter pools *versus* holocellulose litter pools during decomposition, the parameters controlling these are an important area for further examination and refinement. Measurements of microbial products or using changes in DOC C/N ratios to determining plant litter versus microbially-derived DOC through time would address these remaining uncertainties regarding LIDEL simulations of microbial processes.

Another area for further development in the LIDEL model is the relationship between N availability and microbial biomass characteristics (e.g. fractionation between soluble *versus* structural material with microbial biomass turnover). For example, is the partitioning of microbial biomass between soluble and non-soluble products controlled by N availability? N control of microbial generation of DOC versus microbial products can be simulated by the LIDEL model but was not a

hypothesis we could explore given the data used in this analysis. However, this is potentially an important consideration for stabilization of litter inputs in soils due to N effects on microbial processes.

The hierarchical Bayesian approach used to estimate LIDEL parameters in this analysis suggests the importance of examining the relationship between measures of soluble plant litter fractions and variability in the true plant litter soluble fractions both within and across litter types. As discussed above, the soluble plant litter pool is conceptually well defined but more difficult to measure in a way that links to its ecological function and variability. Measurement of the soluble pool using HWE is clearly more variable than measurement by mass-difference (Figure 3-5, A & B). However, both types of measurements are variable relative to the estimated true state of the soluble fraction (Figure 3-5, C), making it difficult to determine whether one or the other more accurately reflects the true litter soluble fraction, or if another measure of the litter soluble fraction would be more consistent. The results of this analysis support the importance of the soluble litter fraction in both generating DOC and driving microbial dynamics during litter decomposition. Comparative measures of a variety of litters from a variety of sources, using both analysis techniques, is needed to clarify the connection between soluble litter C, measurements of soluble litter fractions, and the generation of DOC *versus* persistent microbial products during litter decomposition.

In the IC analysis we estimated an entirely unknown model parameter: f_{DOC} , or the fraction of soluble plant litter that avoids microbial processes and is immediately released from plant litter when it is exposed to water. In our IC analysis we informed the estimate of initial DOC using the cumulative DOC measured from day 0 – day 10 of the Soong et al. (2015) experiment. As shown in Table 3-2, this fraction estimate has the broadest 95% BCI width, likely in part due to a lack of any direct measurements as well as the estimation of one single initial DOC fraction across all litter types. We observed that the use of this parameter distribution to initialize the pine DOC pool from the Soong et al. (2015) experiment in the TD analysis resulted in initial DOC estimates that were higher than DOC ever cumulatively reached in the

experiment. We therefore added a ‘structural protection’ coefficient (0.4) for pine initial DOC, based on the assumption that needle litters have a molecular structure that allows for a greater protection of plant soluble C. This suggests the need to examine factors that physically protect soluble C from leaching, in addition to the microbial processes reflected in the generation of DOC in the LIDEL model. Litter-specific initial f_{DOC} parameters may need to be estimated to better reflect litter-specific variability in this OM fraction.

DOC showed its highest measured values early in the decomposition experiment, with the majority of leachate accumulating within the first few weeks. Simulating these high early fluxes is important from the standpoint of accurately modeling the largest litter inputs into soils, further supporting closer examination of the f_{DOC} parameter. It is also important to accurately simulate overall litter decomposition dynamics (i.e. mass remaining), as undecomposed litter can be an increasingly important contributor to SOM formation in late stages of decomposition (Cotrufo et al., in review, Nature Geosciences). The results of this analysis statistically support Model 1 as the best fit given the data (RMSE values, Table 3-3). However, litter contributions to soils would likely be more accurately simulated by a LIDEL model formulation more in the direction of Model 2, in terms of simulating the generation of the products of litter decomposition with the potential to make the greatest contributions to SOM dynamics. Therefore, further development of the LIDEL model should focus on simulating these key periods in litter decomposition, in order to more accurately reflect the connection between litter decomposition, the generation of products from litter decomposition, and SOM dynamics.

3.5 Conclusions

In this analysis we present the LIDEL model, a new litter decomposition model that includes dynamic lignin and N controls on microbial CUE and simulates the partitioning of litter decomposition products to DOM, CO₂, microbes, and microbial products. By simulating the production of these dissolved and particulate litter C products, the LIDEL model can more accurately connect litter

decomposition with important SOM C input pathways identified in litter decomposition experiments (e.g. Cotrufo et al., in review, Nature Geosciences), but poorly represented in many SOM models (e.g. Schmidt et al., 2011). We use hierarchical Bayesian methods to inform LIDEL model parameters with experimental and literature-derived data, both for initial LIDEL conditions as well as parameters that drive LIDEL temporal dynamics. Some parameters were informed by the data more strongly than others, due to variability in the measured data as well as the strength of the linkage between measurements and conceptually defined LIDEL model pools. The LIDEL model provides a robust theoretical structure to connect litter chemistry to microbial processes and the generation of products from litter decomposition, suggesting testable hypotheses for controls on microbial processes and their connection to the generation of products from litter decomposition.

Table 3-1 Litter chemistry characteristics from Soong et al. (2015).

Litter	Average initial %N	Initial L_c range
Alfalfa (<i>Medicago sativa</i>)	4.09	0.15-0.42
Ash (<i>Fraxinus excelsior</i>)	0.88	0.28-0.64
Bluestem (<i>Andropogon gerardii</i>)	0.48	0.22-0.64
Oak (<i>Quercus macrocarpa</i>)	1.32	0.48-0.86
Pine (<i>Pinus ponderosa</i>)	0.41	0.51-0.80

Table 3-2 Estimated parameters for fractions used to initialize LIDEL model pools, reporting mean and 95% Bayesian credible intervals as well as credible interval widths.

Fraction	Litter	Mean	95% BCI	95% BCI Width
DOC	All	0.15	0.09-0.21	0.12
Soluble C	Alfalfa	0.70	0.65-0.75	0.11
	Ash	0.52	0.46-0.58	0.11
	Bluestem	0.27	0.22-0.33	0.11
	Oak	0.40	0.35-0.45	0.11
	Pine	0.35	0.29-0.40	0.11
Lignin C	Alfalfa	0.08	0.05-0.12	0.07
	Ash	0.15	0.11-0.18	0.08
	Bluestem	0.13	0.09-0.16	0.07
	Oak	0.27	0.23-0.31	0.08
	Pine	0.32	0.28-0.38	0.08

Table 3-3 Mean and 95% Bayesian credible intervals for the five estimated LIDEL parameters, as well as mean root mean square error for LIDEL model predictions versus out-of-sample measurements for each iteration of the TD analysis after the burn-in period.

		Model 1		Model 2		Model 3		Model 4	
N Limitation Curve:		Logistic		Logistic		Linear		Linear	
DOC/CO₂ Frac.: Sol vs Holo:		Equal		Soluble Higher		Equal		Soluble Higher	
Parameter	Definition	Mean	95% BCI						
k_1	Soluble decay	0.24	0.13-0.50	0.37	0.16-0.70	0.097	0.038-0.23	0.28	0.071-0.93
k_2	Holocell. decay	0.0079	0.0016-0.017	0.0090	0.0011-0.020	0.0034	0.0015-0.0067	0.0049	0.0018-0.012
k_4	Mic. biomass decay	0.60	0.14-0.97	0.57	0.11-0.97	0.55	0.071-0.97	0.51	0.053-0.97
β_3	Mic. prod. from mic. biomass	0.27	0.022-0.76	0.33	0.028-0.77	0.50	0.048-0.92	0.43	0.042-0.88
λ_2	DOC from mic. biomass	0.16	0.018-0.41	0.19	0.022-0.42	0.063	0.0092-0.23	0.099	0.011-0.32
RMSE		15280		16150		15350		17380	

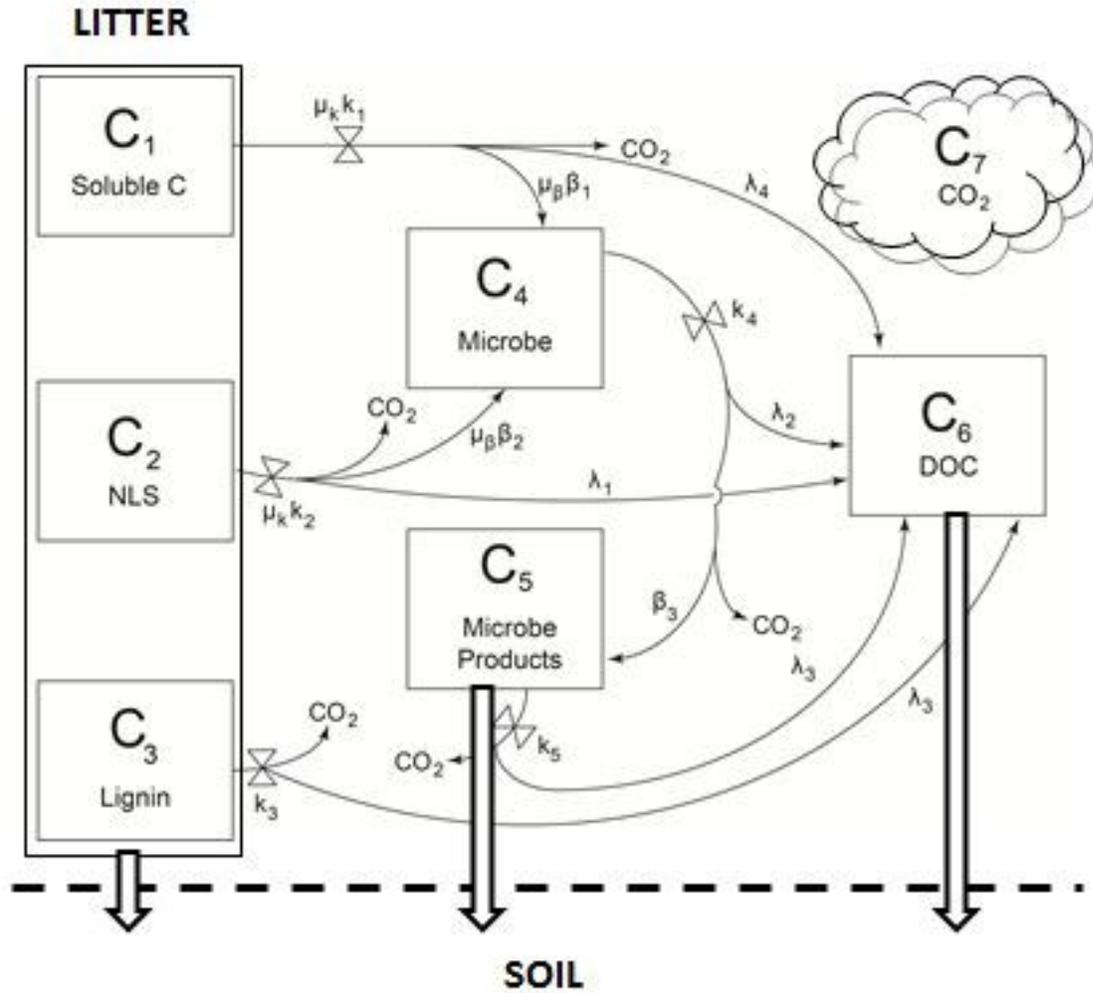


Figure 3-1 Schematic showing the soluble (C₁), non-lignin structural (C₂), lignin (C₃), microbial biomass (C₄), microbe products (C₅), DOC (C₆), and CO₂ (C₇) pools within the LIDEL model, in addition to the fluxes that connect model pools and the parameters that control the rates of these fluxes. The three litter pools (C₁, C₂, and C₃) generate microbial products (C₅) and DOC (C₆) as separate physical pools that, alongside remaining litter, can then enter soils and soil organic matter formation pathways.

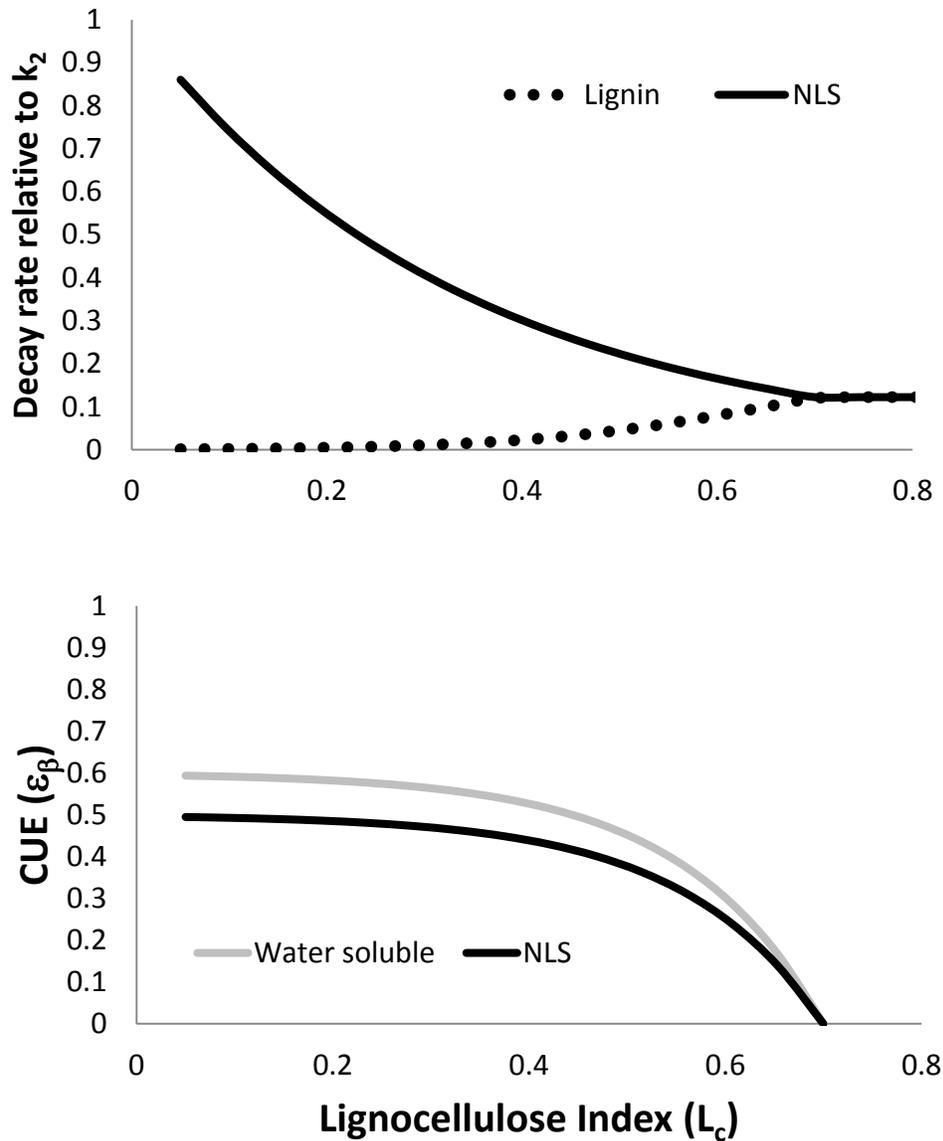


Figure 3-2 Limitation on water soluble and holocellulose decay rate (A), and microbial CUE with use of these litter fractions (B), by lignocellulose index. Water soluble litter is assumed to have a maximum CUE closer to the theoretical maximum of 0.6 proposed by Moorhead et al. (2013), while holocellulose (NLS) is proposed to have a lower maximum of 0.5. Equations modified from those presented in Moorhead et al. (2013) to be expressed as a single continuous non-linear equation rather than the combination of linear equations (Moorhead et al., 2013).

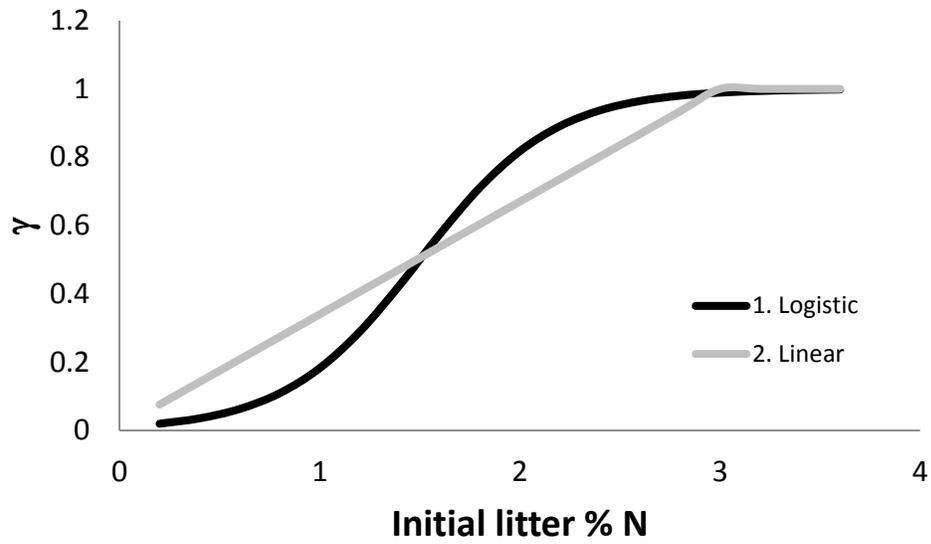


Figure 3-3 Limitation on CUE and decay of water soluble and holocellulose pools by initial litter percent N, as based on a 3% threshold element ratio drawn from (Sinsabaugh et al., 2013).

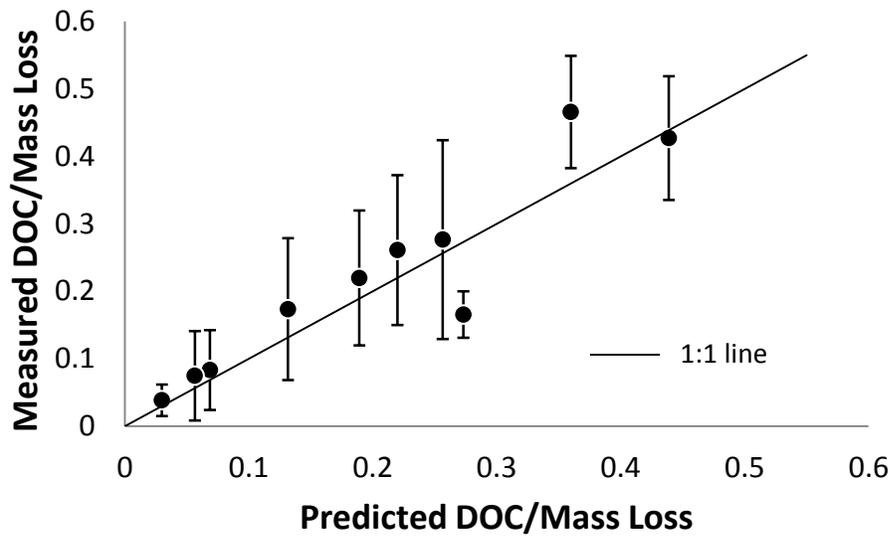


Figure 3-4 Measured versus predicted DOC generation per mass lost during decomposition, taking the minimum of the predicted fractionation based on % initial N and initial L_c , for early and late-stage decomposition.

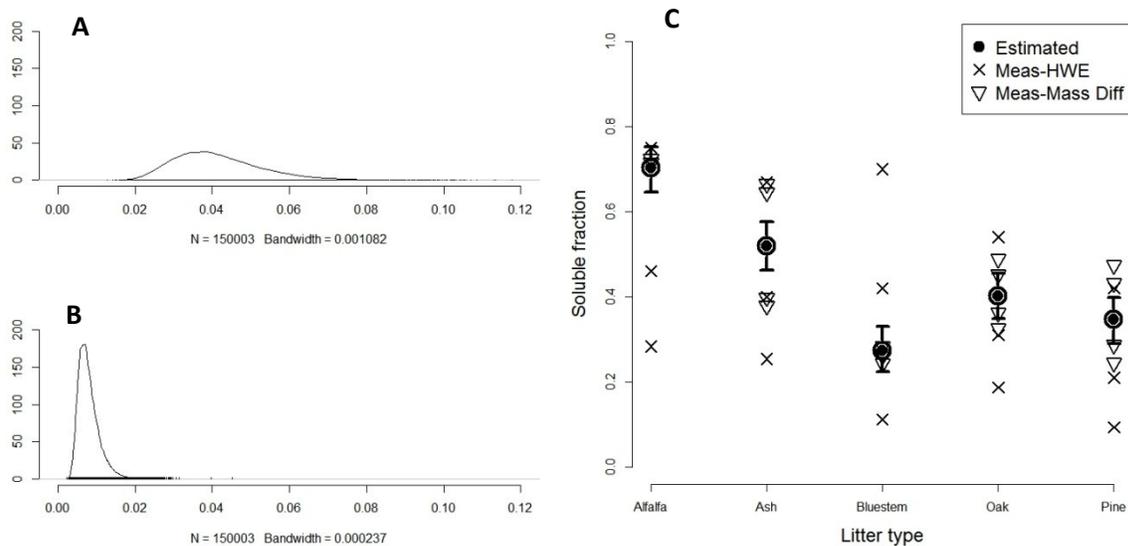


Figure 3-5 Initial Condition Bayesian analysis results, showing trace density plots of estimated variance parameters for hot water extraction (A) and mass-difference (B) measurements of the litter soluble fractions, as well as the final estimate of the soluble fraction parameters (showing means and 95% Bayesian credible intervals) by litter type as compared to measured values (C).

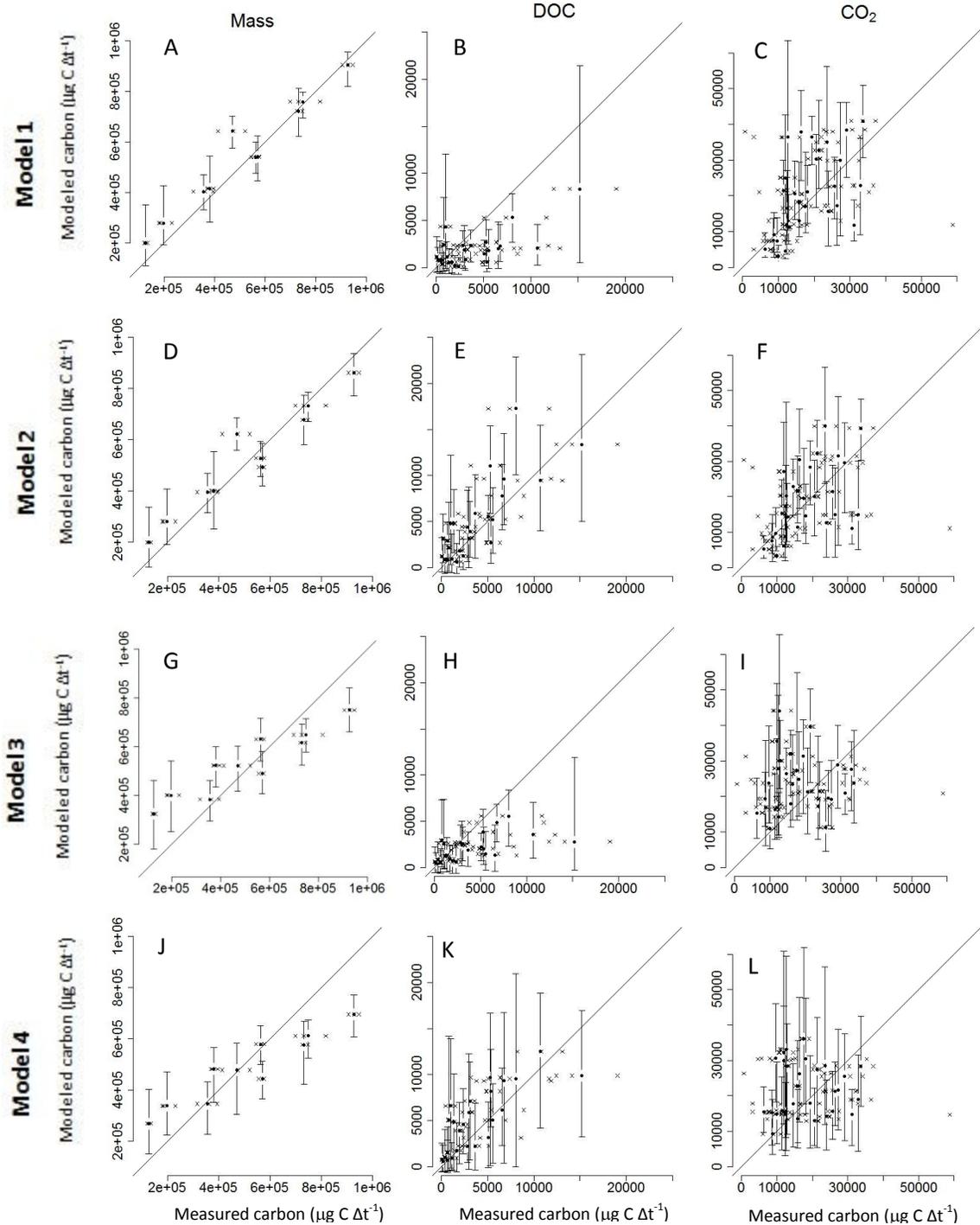


Figure 3-6 Measured (x-axes), versus modeled (y-axes) LIDEL prediction of litter mass remaining (A, D, G, & J) as well as the generation of DOC and CO₂ (B & C, E & F, H & I, K & L) for the four model formulations evaluated in the TD hierarchical Bayesian analysis, presenting posterior means (dark circles) and 95% BCIs for each LIDEL prediction of measured data. Diagonal lines indicate 1:1 relationships.

4 ASSESSING THE SOIL CARBON, BIOMASS PRODUCTION, AND NITROUS OXIDE EMISSION IMPACT OF CORN STOVER MANAGEMENT FOR BIONERGY FEEDSTOCK PRODUCTION USING DAYCENT³

4.1 Introduction

Corn (*Zea mays* L.) stover, the plant residue remaining after harvest, is an attractive source of biomass for bioenergy in the United States (US). The US Department of Energy Billion Ton Study Update (2011) considers agricultural residues such as corn stover to be among the best sources of raw material to support bioenergy industry, as they are already produced on a large scale at low costs in regions with established crop production infrastructure. Corn stover currently accounts for ~70% of all crop residue production in the US and is therefore of high interest as a feedstock to support the expansion of industrially-scaled bioenergy production (U.S. Department of Energy, 2011).

The impetus to expand bioenergy production in the US, exemplified at the federal level with the Energy Information and Security Act of 2007 and its revised Renewable Fuels Standard (RFSII), includes replacing the use of fossil fuels to strengthen US fuel security, reduce the climate change impact of fossil fuel combustion, and concomitantly enhance rural development (Lynch and von Lampe, 2011).

However, the removal of crop residues to expand bioenergy production must consider potential impacts to the agroecosystem services provided by agricultural byproducts like corn stover. While corn stover is widely available in the corn production regions in the US, care must be taken with residue removal in order to maintain agroecosystem health and productivity (Halvorson and Jantalia, 2011; Karlen et al., 2011b). Crop residues influence multiple agroecosystem functions which impact crop productivity, including providing the building blocks for soil organic matter that in turn contribute to water and nutrient-holding capacity as well as nutrient availability (Burgess et al., 1996; Linden et al., 2000; Power

³ Campbell, E.E., Johnson, J.M.F., Jin, V.L., Lehman, R.M., Osborne, S.L., Varvel, G.E., Paustian, K., 2014. Assessing the Soil Carbon, Biomass Production, and Nitrous Oxide Emission Impact of Corn Stover Management for Bioenergy Feedstock Production Using DAYCENT. *BioEnergy Research* 7, 491–502. doi:10.1007/s12155-014-9414-z

et al., 1986). Crop residues can reduce soil erosion, help maintain soil fertility, and impact greenhouse gas emissions (GHGs), including nitrous oxide (N₂O) and methane (CH₄) fluxes from soil and changes in soil organic carbon (SOC) storage and net carbon dioxide (CO₂) emissions (Crutzen et al., 2008; Wilhelm et al., 2004). Corn stover removal can reduce or increase grain yields depending on other land characteristics and management practices (Burgess et al., 1996; Varvel et al., 2008). Furthermore, replacing nutrients removed by stover removal can increase fertilizer costs (Karlen et al., 2011a). Sustainable agricultural management practices involving residue use must support a robust bioenergy industry, meet climate impact reduction (e.g. RFSII) standards for renewable fuels, and maintain cropland health to support growing crop production demands.

An economically viable and environmentally sustainable bioenergy industry based on corn stover feedstock must incorporate both crop management practice recommendations for corn stover production as well as accurate predictions of production potential. Past studies evaluated impacts of corn stover removal on subsequent grain yield (Burgess et al., 1996; Maskina et al., 1993; Power et al., 1986; Wilhelm et al., 1986), and used long-term sites to address other ecosystem effects such as SOC changes (Hooker et al., 2005; Moebius-Clune et al., 2008; Wilts et al., 2004). A research goal of the Sun Grant Initiative's Corn Stover Regional Partnership team- which is also supported by the USDA-Agricultural Research Service's Resilient Economic Agricultural Practices (ARS-REAP) project- was to supplement these studies by establishing an extensive network of field trials across a range of climatic and soil types to assess varying levels of residue removal on soil C, water, nutrient content, as well as biomass characteristics. More information on the Regional Partnership studies are included within this and previous publications (Karlen, 2010; Karlen et al., 2011a, 2011b).

The Regional Partnership corn stover trials greatly expand of the amount of site-specific primary data on corn stover residue production and the agroecosystem impacts of its removal. Empirical data are needed to calibrate, validate, and refine process-based models so they can be used to help establish

valid sustainable harvest rate guidelines (Johnson et al. (this issue) and (Wilhelm et al., 2004)). The need for such data was recognized by the Regional Partnership corn stover team; therefore the project was designed to support predictive modeling, linking field trial data to expanded regional projections (Karlen, 2010).

A modeling tool suited to accommodate region-specific factors and provide regional predictions for a broad array of agroecosystem impacts is DAYCENT. The DAYCENT model, a process-based ecosystem model developed at Colorado State University, simulates GHG fluxes as well as plant/soil C dynamics and many other ecosystem processes (Parton, 1988, 1987). DAYCENT and its predecessor CENTURY have been applied and tested in many agricultural systems both in the US and globally (Abdalla et al., 2010; Del Grosso et al., 2008; M. V. Galdos et al., 2009), including several types of bioenergy production systems (Adler et al., 2007; Davis et al., 2012, 2010). While DAYCENT modeling of corn production has been widely tested for model applications such as estimating agricultural land use emissions for the US Environmental Protection Agency annual GHG inventory report (U.S. Environmental Protection Agency, 2013), evaluations of its performance simulating the impacts of corn stover harvest are limited. One example is a recent study by Gao et al. (2013), where DAYCENT was applied as part of a Michigan-specific life-cycle assessment (LCA) of corn stover management (Gao et al., 2013).

There is a critical need for the application of process-based models such as DAYCENT in designing scientifically sound decision support tools for the development of bioenergy feedstock production (Huggins et al., 2011). Therefore, members of the Regional Partnership team completed a review to identify economic and sustainability metrics that impact the potential for corn stover residue harvest in the Midwest (Wilhelm et al., 2010). Based on this review (Wilhelm et al., 2010), an integrated stover removal tool was designed that linked several existing models (i.e. the Revised Universal Soil Loss Equation Version 2 (RUSLE2), the Wind Erosion Prediction System (WEPS) and the Soil Conditioning Index (SCI)) to predict maximum residue removal rates that would meet multiple sustainability criteria

(Muth and Bryden, 2013). Recently, the DAYCENT model was integrated into this framework to provide dynamic estimates of biomass yields, SOC changes and GHG fluxes, thereby refining the evaluation and recommendation of 'sustainable' residue removal rates on regional and site-specific levels. Evaluating DAYCENT simulations of corn stover residue removal effects against empirical data from the Regional Partnership field sites contributes to the development of the sustainability assessment tool that can provide region-specific recommendations to support agroecosystem services and the bioenergy industry.

Balancing agroecosystem services and developing a viable large-scale bioenergy industry will require changing management practices (e.g., growing cover crops, modifying fertilizer form or rate) to increase or supplement C and nutrients in the system. Cover crops and manure application (Fronning et al., 2008; Wiggans et al., 2012), increased synthetic N fertilizer application (Sindelar et al., 2013, 2012), and reduction in tillage intensity (Hooker et al., 2005; Linden et al., 2000) have been identified as amelioration approaches to develop 'sustainable' practices for corn residue harvest (Gollany et al., 2010; Wilhelm et al., 2010) and subsequently are recurring focal treatments in field studies assessing corn stover management. In this study, we evaluated DAYCENT performance in simulating SOC change, corn grain and stover yields, and direct N₂O emissions- a powerful greenhouse gas (Forster, 2007)- from soils against measured data from three of the Regional Partnership corn stover sites and two long term published corn stover removal experiments (Clapp et al., 2000; Follett et al., 2012; Hammerbeck et al., 2012; Linden et al., 2000; Reicosky et al., 2002; Stetson et al., 2012; Varvel et al., 2008; Wilts et al., 2004). For the current study, simulated treatments were based on site-specific variation in residue removal rates, tillage, N fertilizer and cover crops. We focus our analyses on overall DAYCENT performance in these systems, as well as on the measured versus modeled impacts of residue removal rates combined with variation in tillage treatments.

4.2 Materials and Methods

4.2.1 Experimental Data

To test the performance of the DAYCENT model, a series of data were assembled from published literature evaluating two sites in Rosemount, MN and Morris, MN for the soil and crop production impacts of long-term corn stover removal, as well as different levels of nitrogen (N) fertilizer application and types of tillage (Clapp et al., 2000; Linden et al., 2000; Reicosky et al., 2002; Wilts et al., 2004). Data were also assembled from three Corn Stover Regional Partnership sites in Ithaca, NE, Brookings, SD and a different site in Morris, MN established as a subset of ARS-REAP to evaluate the sustainability of corn stover harvest (Karlen, 2010). The Regional Partnership sites test multiple levels of residue removal combined with differences in tillage, N fertilizer application, and cover crop management practices and are described in greater detail in this issue as well as in prior publications (Hammerbeck et al., 2012; Stetson et al., 2012; Varvel et al., 2008). Measurements at the Regional Partnership sites included grain and stover yields, SOC change from 0 – 20 cm, and direct soil N₂O emissions (Table 4-1). The Regional Partnership data and published literature values allowed us to test DAYCENT's performance in simulating biomass (i.e. grain and stover) production, SOC change, and N₂O emissions.

4.2.2 DAYCENT Model Overview

The DAYCENT model runs on a daily time-step and simulates various ecosystem processes to a soil depth of 20 cm. The model includes routines for simulating the movement of soil nutrients, the movement of water through soil layers, plant growth, and many other ecosystem components that are described in greater detail elsewhere (Del Grosso et al., 2008). The key drivers of DAYCENT include maximum and minimum daily temperature, daily precipitation, soil texture, and land management (including specific plant types grown and soil management such as tillage and nutrient additions).

The DDcentEVI version of DAYCENT (a version of DAYCENT with the option to use Enhanced Vegetation Index- i.e. EVI- data) was used for this analysis. DDcentEVI was developed and tested to estimate total agricultural land use emissions for the US Environmental Protection Agency's (EPA) GHG emission inventory annual report (U.S. Environmental Protection Agency, 2013). This repeated annual set of simulations involve model parameterization for common agricultural crops- including corn and soybean- as well as millions of model runs and established protocols for estimating model uncertainty (Del Grosso et al., 2010; Ogle et al., 2010, 2007), documented in detail in Annex 3.12 of the most recent inventory report (U.S. Environmental Protection Agency, 2013). Given the extensive parameterization process with DDcentEVI, we chose to use this version in order to focus our efforts on validating model performance using all data for corn stover residue removal experiments available for this analysis.

An important component of any DAYCENT model simulation is initializing the model based on the native ecosystem type expected for the specific site and using the best available information about land management after the native ecosystem is converted for agricultural use. Given temperature and precipitation as key drivers of biogeochemical processes, the longest possible continuous daily climate datasets are needed to run model initializations as well as drive simulations for the experimental periods of interest. The climate data used to drive model simulations for this study were derived using the latitude and longitude of site locations to determine the nearest North American Regional Reanalysis (NARR) grid cell and the associated daily maximum and minimum temperatures and total precipitation from 1979 – 2009. NARR data, given at a 32 km scale, were generated as an extension of the National Centers for Atmospheric Research Global Reanalysis project and are freely available online (<http://www.emc.ncep.noaa.gov/mmb/rrean/>). NARR data are generated using algorithms to interpolate weather for areas between weather stations. The NARR dataset is the standard used for simulations in the US GHG inventory, and therefore was the source of climate data for all sites and years in this analysis where site-specific data were not available. For the three Regional Partnership sites, site-

specific daily weather data were available for the experimental time periods, and these data were used instead of NARR weather data in the years available, extending the climate data time period at these sites to 2010.

Soil texture information was gathered either from direct field measurements reported by the Regional Partnership sites or from soil texture data reported in publications for the two non-Regional Partnership sites. Prior land use history used for model initialization were drawn from 1) county-level native vegetation assumptions used in simulations for the EPA GHG emission annual report and 2) information gained from literature and personal communication for agricultural management from when native vegetation was converted into cropland up to the treatment period. Experimental management practices, such as planting and harvest dates, dates and quantities of fertilizer application, and corn stover harvest rates, were drawn from reported literature and Regional Partnership field data. These land use data were used to schedule events within DAYCENT model simulations. A total of 53 different corn stover management scenarios, matching experimental management practices across the five experimental sites, were simulated to generate model results to compare against measured data.

4.2.3 Statistical Analyses

Statistical analyses were completed using R-2.15.1 software as well as the Hmisc and car packages (Fox and Weisberg, 2011; Harrell Jr., 2012; R Core Team, 2012). Regression analyses were applied to compare measured versus modeled grain yield (Mg C ha^{-1}), stover yield (Mg C ha^{-1}), SOC change over the measurement period (Mg C ha^{-1}), and annual N_2O flux ($\text{kg N}_2\text{O-N ha}^{-1} \text{yr}^{-1}$) across all sites and all years. Two treatment effects were also selected for measured versus modeled estimate evaluation: (1) residue removal level, and (2) residue removal level + tillage. For measurements taken across multiple years, averages by treatment were used to compare measured versus modeled results across all sites. For evaluation of residue removal level alone, measured versus modeled estimates of grain C and SOC change were compared for three stover removal levels: full removal (100 %), moderate

removal (29 – 50%), and no removal (0%). Soil N₂O emissions were evaluated using two treatment levels: stover removal (>0%) and no removal (0%). For evaluation of residue removal level + tillage, measured versus modeled estimates of grain C and SOC change were compared using four levels: conventional tillage + 0% removal, conventional tillage + >0% removal, no tillage + 0% removal, no tillage + >0% removal. Measured versus modeled estimates were assessed for normality using a Shapiro-Wilk test, as well as assessed for equal variance. These measured versus modeled estimates were then assessed across these treatment effects using type III sums of squares two-way analyses of variance (ANOVAs) to account for unequal sample sizes, where the fixed effects tested were residue removal level and tillage.

4.3 Results

4.3.1 Biomass

DAYCENT simulated annual grain yields with significant correlation with measured yields but with high dispersion and significant bias – there was a significant positive intercept and a slope less than 1 (Figure 4-1a). DAYCENT simulated annual stover harvest with a tighter significant correlation and less bias, with a slope closer to 1 and an insignificant intercept (Figure 4-1b).

Measured and modeled average grain yields across sites did not differ between residue removal levels (Figure 4-2a, $p>0.05$). Across all treatment levels, measured values were significantly higher than modeled estimates (Figure 4-2a, $p=0.012$). Measured and model estimates of average grain yields did not show a significant overall effect of tillage + residue removal levels, measured versus modeled estimates, or a significant interaction between these factors (Figure 4-2b, $p>0.05$).

4.3.2 Soil C Change

Modeled and measured SOC change for all sites exhibited a significant correlation but deviation from the 1:1 linear relationship, with a significant positive intercept and slope less than 1 (Figure 4-3a). Excluding sites that had ten or fewer years between initial and final SOC measurements (Figure 4-3b),

and thus greater uncertainty in the magnitude and direction of change, gave a tighter correlation between measured and modeled estimates. However, removing short-term sites did not change the model overestimation of SOC loss rates for sites where measured SOC stocks were declining, with a less significant positive intercept and a lower slope (Figure 4-3b).

For treatments where the time between initial and final SOC measurements exceeded 10 years, SOC change did not vary significantly by residue removal rate or by the interaction between residue removal rate and the measured versus modeled estimates (Figure 4-4a, $p > 0.05$). However measured versus modeled estimates did differ significantly, with the model consistently overestimating SOC change in the same direction as the measured data (Figure 4-4a, $p < 0.001$). For these same treatments, SOC did vary significantly by tillage + residue removal level and measured versus modeled estimates alone, as well as by the interaction between these factors (Figure 4-4b, $p = 0.003$, $p = 0.003$, and $p = 0.006$, respectively). Both the measured and modeled data suggest conventional tillage leads to a loss of SOC, while no tillage leads to a gain or little change in SOC that may depend on whether residue is removed. However the model shows a clear bias of overestimating SOC loss with conventional tillage, with or without residue removal.

4.3.3 N₂O emission

Modeled versus measured annual N₂O emissions showed a significant relationship and an intercept that did not differ significantly from 0, but the slope > 1 indicates a model bias of underestimating annual N₂O emissions. The increasing divergence from the 1:1 line between modeled and measured values with higher measured emission rates suggests better DAYCENT performance in low-emission systems ($< 2 \text{ kg N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$) but underestimation for sites and years with high emission rates (i.e., $> 3 \text{ kg N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$) (Figure 4-5a). There were no significant differences in N₂O as a function of residue removal in either the measured or modeled estimates (Figure 4-5b, $p > 0.05$ for all factors).

A qualitative comparison of measured versus modeled estimates of daily N₂O emission shows no obvious pattern of divergence between daily modeled and measured values when N₂O emissions are low (Figure 4-6 & 7). However there is substantial divergence when N₂O emissions are in peak periods. DAYCENT sometimes simulated peak periods with similar timing to measured peak periods but underestimated their magnitude (Figure 4-6b, Figure 4-7c). DAYCENT simulation of peaks sometimes did not match the timing of measured peaks (Figure 4-6d, Figure 4-7b). DAYCENT also failed to simulate some peak periods reflected in the measured data (Figure 4-6b, Figure 4-7a & 7b).

4.4 Discussion

4.4.1 Biomass

Modeled results suggest that DAYCENT can reasonably simulate corn stover yields across the management practices considered in this study, a key concern for the expansion of bioenergy industry based on corn residue as a feedstock material. However the slope did exceed 1- the value that would reflect perfect model simulation of measured values- indicating some bias towards DAYCENT underestimating stover yields that should be considered in the use of DAYCENT model results within the context of a bioenergy decision support tool.

DAYCENT performed more poorly in simulating annual grain yields. The low coefficient of determination (r^2) reflected high dispersion, and the model tended to overestimate grain yields in years where measured grain yields were low and underestimate grain yields in years where measured grain yields were high (Figure 4-1a). DAYCENT simulates the growth of aboveground biomass based on interactions between moisture and temperature, and then simulates grain harvest based on the harvest index specified by the user. Fine-scaled timing-specific interactions between temperature, moisture, and grain yields (e.g. high or low precipitation or temperature events that impact flowering or grain filling) are not yet included in DAYCENT, and may cause its variable performance simulating annual grain yields. When the data were aggregated across years, DAYCENT did successfully simulate the overall non-

significant impact of corn stover residue removal levels across these treatments; however, the significant difference between modeled versus measured results indicates an overall model bias of underestimating grain yields (Figure 4-2a). This bias was not apparent in the comparison between measured versus modeled grain yields across combined tillage and residue removal levels; in this analysis, the model successfully captured the overall insignificant impact of residue removal levels and tillage on grain yields, with no significant difference between measured and modeled results (Figure 4-2b).

These results suggest DAYCENT can be used to successfully model the relative impacts of residue removal on grain yields, but should be used carefully if simulating quantities of grain yield on an annual basis. The DDcentEVI version of DAYCENT has shown a tendency to overestimate water stress effects on grain production in the northern Midwest region (Steve Williams, personal communication). This region was the location of several sites used in this study that showed substantial model underestimation of annual grain yields relative to measured values (open circles, Figure 4-1a). This model bias should be addressed for evaluating sustainability factors for corn stover residue harvest in the northern Midwest region, with a better representation of water stress effects on grain yields- particularly better representation of the effects of precipitation timing, which can be critical for grain production- to alleviate this bias in modeled results.

4.4.2 Soil C change

The DAYCENT model had variable performance modeling SOC change. DAYCENT simulations matched the direction of SOC change for most sites (Figure 4-3a), particularly sites with greater periods of time between initial and final SOC measurements used to calculate SOC change (Figure 4-3b). DAYCENT results, however, showed increasing divergence from measured values showing SOC losses (Figure 4-3). Soil C is highly heterogeneous and variable, and often longer periods of time are required to effectively measure and observe SOC changes due to changes in land management. The sites in this

study with shorter time sets had greater measured variation than was reflected in the model estimates, which tended to model treatments at these sites as just above or below 0 change (Figure 4-3a). It would be useful to repeat measurement of SOC at these sites in the future to assess the accuracy of model simulations over a longer time period. The sites might experience more SOC change following near-term management changes than the model is predicting, but the model might account for some of this SOC change if it simulates the effects of the practice (such as increased decomposition) for longer than the site experiences. Alternatively the model may be underestimating total changes occurring with the management practices at these sites. The modeled versus measured comparison of SOC changes over a longer time period (e.g., 10 years or greater, as were available for the other sites in this analysis) would address this question, with either increasing correlation between measured versus modeled results supporting the former behavior of underestimating near-term changes, or continued disconnect between modeled and measured SOC change indicating poor model performance in these locations. In the latter case, further model assessment of SOC simulations would be required to identify the cause for these site-specific discrepancies in modeled simulations as compared to measured data.

Measured SOC changes by residue removal show no significant SOC change with different levels of residue removal, but suggest greater SOC loss with full residue removal and the potential for SOC gain with partial removal (Figure 4-4a). This supports a number of studies suggesting that SOC change can be minimized by partial rather than full residue removal (Blanco-Canqui and Lal, 2007; Johnson et al., 2010; Varvel et al., 2008; Wilhelm et al., 1986). In contrast, modeled results show the unexpected behavior of greatest SOC gain with moderate residue removal, and potential for loss with both no and full residue removal (Figure 4-4a). However these results could be due to interacting effects with the overestimated modeled SOC loss with conventional tillage, which can be observed in Figure 4-4b.

DAYCENT captures the measured trend of potential for SOC loss with conventional tillage across residue removal treatments versus some SOC gains with residue treatments combined with no tillage

(Figure 4-4b). However the model is clearly overestimating the SOC losses in the conventional tillage treatments (Figure 4-4b). Simulated soil decomposition processes in the DDcentEVI version of DAYCENT may be too sensitive to tillage. Comparison of modeled estimates to total aboveground and belowground biomass, as well as an analysis of modeled soil decomposition sensitivity to tillage, would clarify the model processes causing this overestimation of SOC loss. Despite oversensitivity to tillage, our results support other modeled analyses that identified the potential for no tillage management practices to maintain SOC with residue removal (Dalzell et al., 2013). Specifically, our measured and modeled SOC changes indicated a minimal or positive SOC change when no tillage is combined with residue removal, versus a more strongly negative SOC change when conventional tillage is combined with residue removal (Figure 4-4b). Numerous studies have focused on combining management practices such as increased N fertilizer and reduced tillage with corn stover residue harvest, in order to maintain yields and soil fertility (Burgess et al., 1996; Hooker et al., 2005; Sindelar et al., 2013, 2012). In the set of sites analyzed in this study, we were only able to analyze tillage in addition to residue removal for modeled versus measured analyses. While N fertilizer levels were included in some of the experiments considered in this analysis, aggregating data for cross-site comparison between N fertilizer levels was not possible due to differences in experimental designs. The importance of combined tillage plus residue removal level in this analysis suggests that other combined management practices such as N fertilizer across residue removal levels should be the next focal area of cross-region model validation and assessment, in order to better support the simulation of these management practices within a bioenergy decision support tool framework.

4.4.3 N₂O emission

The DDcentEVI version of DAYCENT performed more accurately modeling lower annual measured estimates of N₂O flux, as indicated by an insignificant intercept in the regression analysis. However the slope indicates increasing underestimation of simulated annual flux as measured values

increased, which is particularly apparent for sites and years $>3 \text{ kg N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$ (Figure 4-5a). Due to how data were reported, error measurements were only available for some of the treatments and were included to give some visualization of the variability of measured annual N_2O estimates (Figure 4-5a). Including error measurements on all measured annual N_2O emission estimates would help clarify the comparison between modeled and measured values. The model showed an overall bias of underestimating annual N_2O flux, when results were averaged and compared across residue removal levels (Figure 4-5b).

N_2O emissions are highly variable and transient, with high flux occurring often in short timeframes following certain events, such as high precipitation, spring-thaw, or N fertilizer application. A comparison of daily measured versus modeled N_2O flux shows that the divergence between measured and modeled annual flux may be due in part to DAYCENT's failure to capture the presence, timing, or magnitude of transient peak periods (Figures 4-6 & 4-7). For example, in the representative treatment shown in Figure 4-6, the model seems to do well in years when soybean is grown and N_2O emissions are consistently low (Figure 4-6, a & c), perhaps missing a small peak around the harvest period. In comparison, when measured values reflect larger and more frequent peaks during corn growth years the model performs more variably. In 2009 (Figure 4-6b) the model simulations seems to match the timing but not the magnitude of the highest N_2O peak and then missed a peak period at the end of the season, while in 2011 (Figure 4-6d) the model simulations seemed to match the magnitude but not the timing of the highest N_2O peak.

Despite evidence for variable DAYCENT performance simulating transient peak periods of N_2O flux, it is challenging to validate DAYCENT performance either cumulatively or on a daily basis using the discontinuous and sometimes sparse time series of N_2O emission measurements made available in this study. These types of N_2O emission datasets are common, as more frequent measurements taken by hand or by automatic chambers are resource-intensive. Where continuous N_2O emission measurements

are not possible, discontinuous samples taken at time points aimed to capture transient periods of high flux as well as background flux across the season is a common methodological approach. However sampling frequency has been recognized to affect cumulative estimates of N₂O emissions, with increasing divergence between true and estimated N₂O emissions as sampling intervals increase in length (Parkin, 2008).

In the comparison between DAYCENT modeled estimated and measured values, when N₂O flux changes occur at a time resolution finer than the measured data, the accuracy of DAYCENT simulation between measured data points will remain unclear. This can be observed in the results of this study, with specific examples include the peaks and lows simulated for N₂O emissions between consecutive high measured data points in Figures 4-6d (measured data on either side of day 200), 4-7a (the first two measured data points), and 4-7b (measured data points on either side of the highest simulated peak). As another example, while the highest measured peak in Figure 4-6d is comparable to the modeled peak in magnitude, it is unknown whether the model is simulating the peak too early, or whether the measurement was taken as the flux was coming down from a higher peak (Figure 4-6).

There is additional potential for sparse, discontinuous N₂O measurements to overestimate annual flux, depending on the resolution and timing of the measured data and the method of integration used to generate an annual estimate. For example, measured time points might miss a peak or a period of low emissions between peaks, or might miss the timing with which a transient peak returns to a baseline flux. The first two data points in Figure 4-7a demonstrate this potential; if the period of low emissions simulated by DAYCENT did occur at that site, but is not considered in the integration of the two measured data points to estimate total flux for that period, their integration will result in an overestimation of N₂O flux. It is possible that DAYCENT's underestimation of high N₂O flux may be due to how the measurement data were integrated to determine cumulative emissions. However it should be noted that a comparison of continuous versus discontinuous N₂O emission

measurements demonstrated a pattern of *underestimation* of cumulative emissions using discontinuous data, due to failure to capture transient peaks in the time interval between measurements (Fassbinder et al., 2013). In this latter case DAYCENT simulations of N₂O emissions would diverge even further from measured estimates in years with high flux. Without data at a higher temporal resolution, it is not possible to determine either the accuracy of the annual measured estimates or the extent to which DAYCENT simulations diverge from true N₂O emissions.

Due the transience and the magnitude of N₂O flux changes across the growing season, there would be great benefits in comparing continuously measured N₂O data against DAYCENT model results, in order to inform the magnitude and timing of peak flux events in model simulations as well as more accurately compare annual flux to measured values. For the purposes of using DAYCENT to evaluate the N₂O emissions of different production practices as a sustainability metric, care should be taken not to underestimate N₂O emissions in systems of potentially high flux.

4.5 Conclusion

Overall DAYCENT had variable performance simulating the impacts of treatments for corn stover harvest included in the 5 sites used in this analysis, with the greatest accuracy simulating corn stover yields and consistency in capturing management practice impacts on the relationship and direction of change with SOC and corn grain biomass. DAYCENT had variable performance simulating N₂O emissions, with more accurate performance where annual emissions are low. Cumulatively the model concurred with measured results suggesting little overall grain yield impacts and suggested the potential for negative SOC impacts with corn stover residue removal and conventional tillage. The model has a tendency to underestimate grain yields- particularly in some regions where the model might be overestimating the impacts of water stress- as well as overestimate SOC loss with conventional tillage, and underestimate treatments with high N₂O emissions compared to modeled data. These behaviors are important to consider when integrating DAYCENT results into a larger sustainability estimate, where

these tendencies could respectively lead to underestimation of corn grain production potential, overestimation of the negative soil C impacts of residue removal and tillage, and underestimation of the emission of N₂O.

Our residue removal and tillage results support the concept of pairing changes in management for corn stover harvest with treatments such as conversion to no-till to maintain productivity and soil health. Modeled results suggested the potential for interactive effects between residue removal and tillage. We also suggest that other combined management practices such as fertilizer application and cover crops be included in subsequent analyses of measured and modeled data comparisons, as these are key practices being considered and recommended as large-scale corn stover harvest for bioenergy moves forward.

This study reflects one of the original purposes of the Regional Partnership corn stover project; integrating field data with predictive modeling of corn stover removal management practices on a regional basis, in order to support the recommendation of sustainable practices to advance a robust bioenergy industry based on corn stover as a feedstock material.

Table 4-1 Summary of study locations and treatments.

Source	Location	Lat/ Long	Management Description	Grain yield	Stover yield	Soil C	N ₂ O
(Reicosky et al., 2002; Wilts et al., 2004)	Morris, MN	45.6/ -95.9	29 years continuous corn; moldboard tillage; low fert. (83 kg N/ha), high fert. (166 kg N/ha), & control (0 kg N/ha); 0 & <i>100% stover removal</i>	X	X	X	-
(Clapp et al., 2000; Linden et al., 2000)	Rosemount, MN	44.7/ -93.1	13 years continuous corn; chisel, moldboard & no till tillage; 0 & 200 kg N/ha; 0 & <i>100% stover removal</i>	X	X	X	-
Reg. Partnership: Swan Lake Exper. Site	Morris, MN	45.7/ -95.8	7 years corn/soy rotation; chisel & no till tillage; 130 kg N/ha; 0, 50, <i>100% stover removed</i>	X	X	X	X
Reg. Partnership: U of N Ag. Res & Develop. Center(Follett et al., 2012; Varvel et al., 2008)	Ithaca, NE	41.2/ -96.4	13 years continuous corn; no till tillage; 60, 120, & 180 kg N/ha; 0 & <i>100% stover removed</i>	X	X	X	X
Reg. Partnership: N. Cent. Ag. Res Lab.(Hammerbeck et al., 2012; Stetson et al., 2012)	Brookings, SD	44.3/ -96.8	7 years corn/soy rotation; no till tillage; avg. 135 kg N/ha; 0, ~29% & ~97% <i>residue removal, with and without cover crop</i>	X	X	X	X

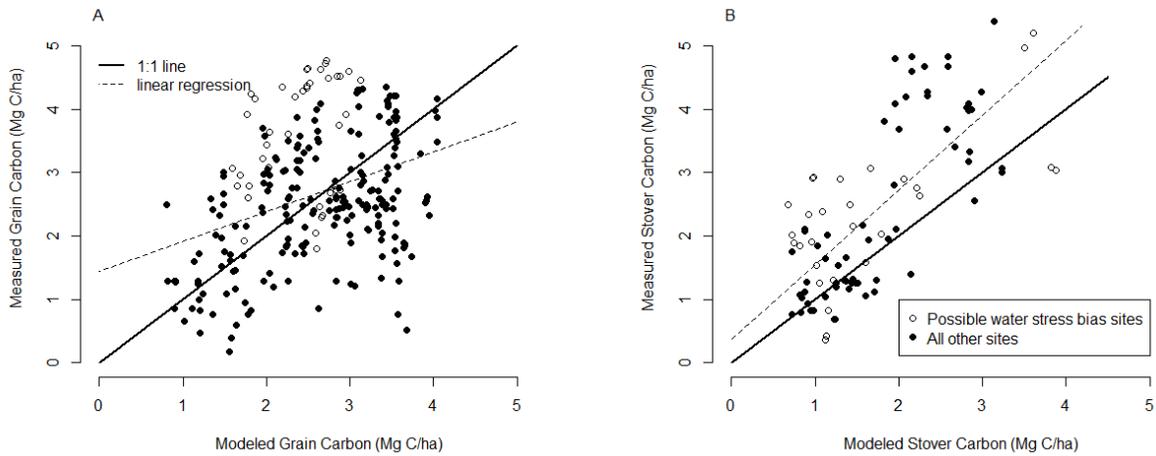


Figure 4-1 Measured versus modeled grain yields (A) and corn stover harvest (B) for all treatments and all years for which daily weather data was available. The grain comparison (A) shows a significant relationship and intercept (adjusted $r^2=0.13$, slope=0.47, intercept=1.43, $p<<0.001$; RMSE=0.95). The stover comparison (B) shows a significant relationship, but insignificant intercept (adjusted $r^2=0.53$, slope = 1.18, $p<<0.001$; intercept=0.36, $p=0.11$; RMSE=0.90).

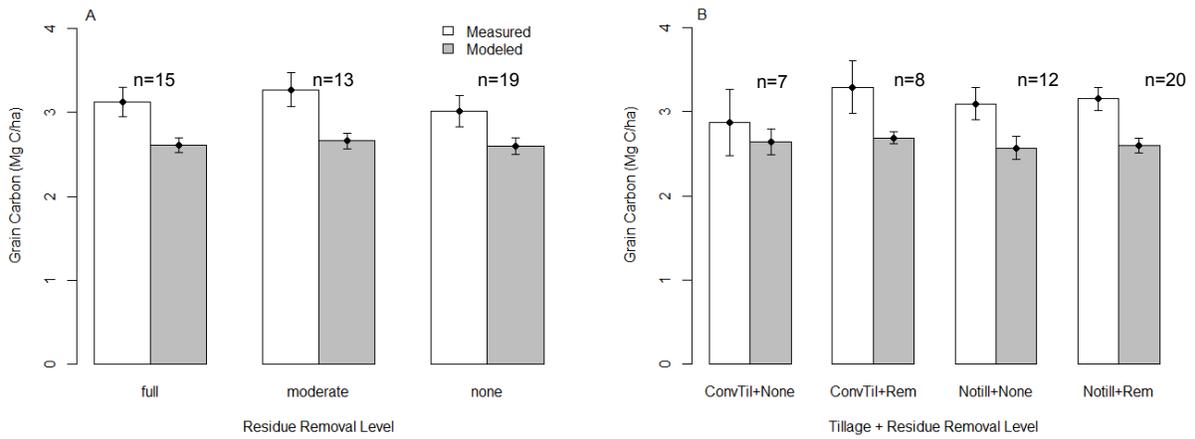


Figure 4-2 Modeled versus measured grain yields by three levels of residue removal rates (100% = full, 100%>moderate>0%, and 0%=none) (A), as well as four levels of combined tillage (conventional versus no tillage) and residue removal (0%=none versus >0%=rem) (B). Error bars show standard error, with the number of replicates reported above each set of measured versus modeled comparison.

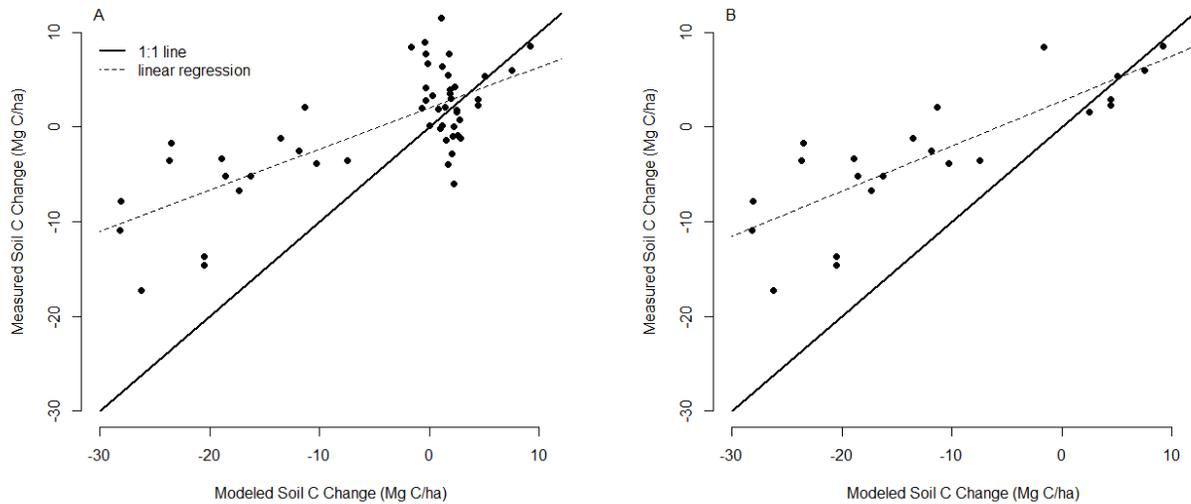


Figure 4-3 Measured versus modeled SOC change from 0 – 20cm for all sites and all treatments (A) and for sites and treatments with greater than 10 years between initial and final SOC measurements (B). All sites (A) show a significant relationship and intercept (adjusted $r^2=0.54$, slope=0.43, $p<<0.001$; intercept=1.97, $p=0.002$; RMSE=4.03). Sites with longer SOC measurements (B) show a significant relationship and slope, but a weakly significant intercept (adjusted $r^2=0.67$, slope=0.48, $p<<0.001$; intercept=2.7, $p=0.03$; RMSE=3.89).

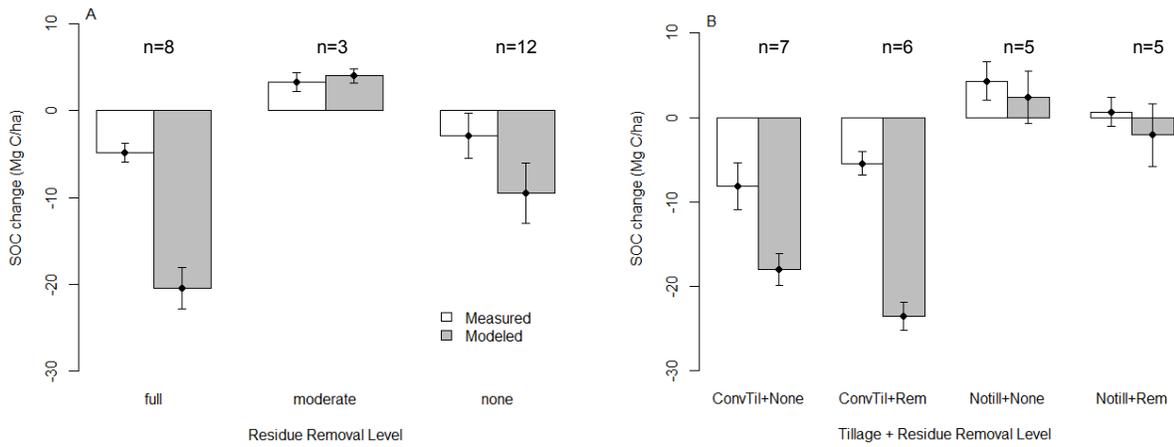


Figure 4-4 Modeled versus measured SOC change at sites with > 10 years between initial and final SOC measurements from 0 – 20cm by three levels of residue removal rates (100% = full, 100%>moderate>0%, and 0%=none) (A), as well as four levels of combined tillage (conventional versus no tillage) and residue removal (0%=none versus >0%=rem) (B), showing standard error.

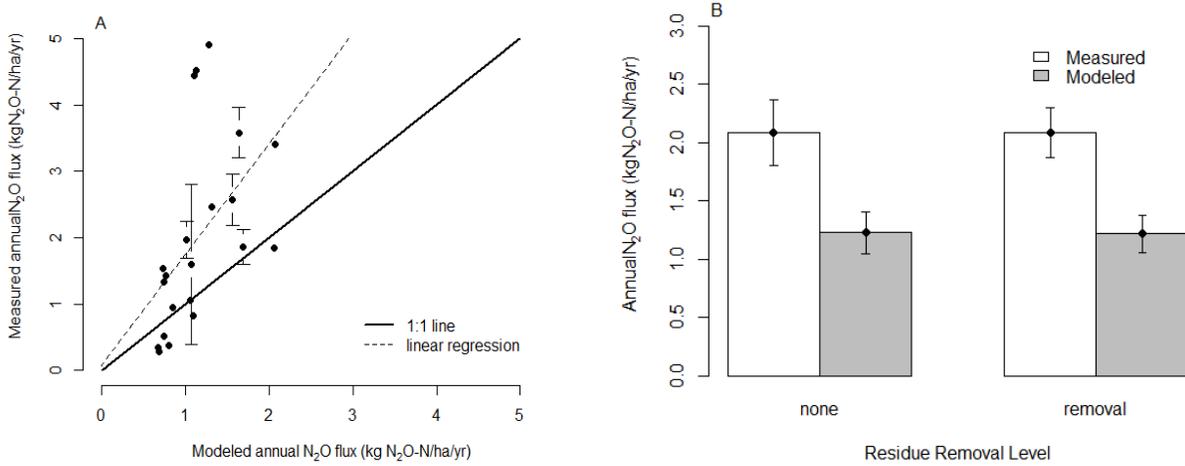


Figure 4-5 Measured versus modeled annual N₂O flux for two sites (A) showing measured standard error where reporting made these data available, a significant relationship, and an insignificant intercept (adjusted $r^2=0.22$, slope=1.67, $p=0.019$; intercept=0.078; RMSE=1.2). Bar graph (B) shows measured versus modeled mean annual N₂O flux by residue removal level (none=0% stover harvest (n=3), removal= >0% stover harvest (n=4)), with standard error.

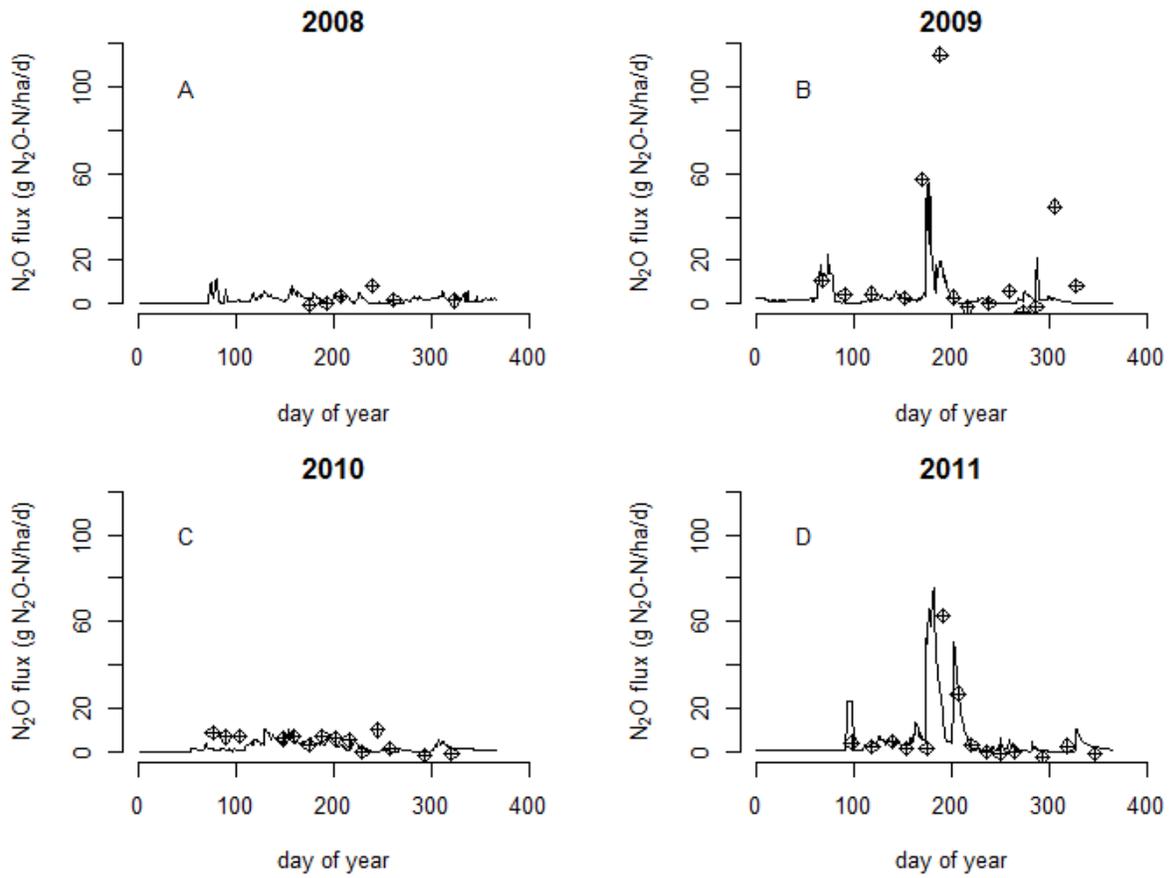


Figure 4-6 Daily N₂O flux measurements (hatched diamonds) compared to daily model simulations (line) of N₂O flux for one representative site under four years of corn - soybean rotation, with no residue removal in soybean years (A and C) partial residue removal during corn years (B and D).

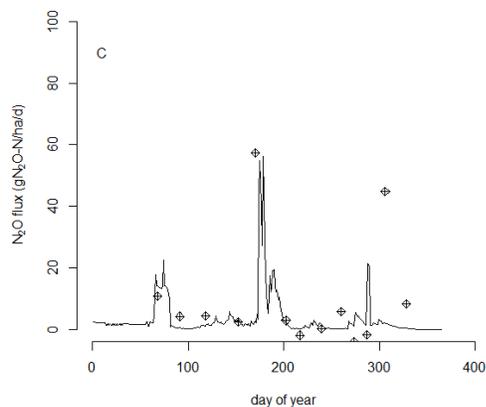
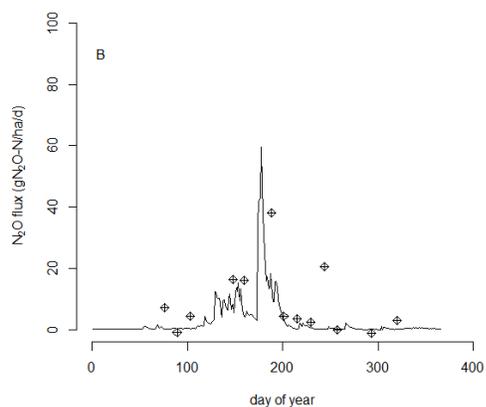
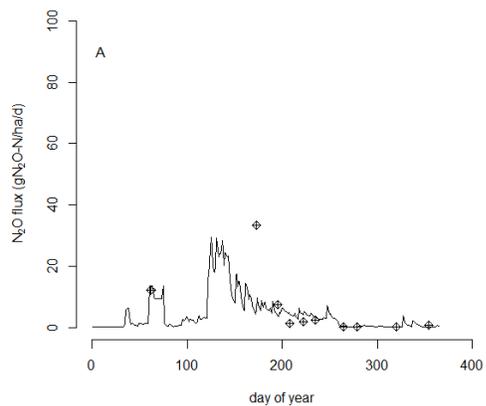


Figure 4-7 Daily measured (hatched diamonds) versus modeled (line) N_2O flux for a selection of sites and years where annual emissions calculated from measured values exceeded simulated annual emissions by at least $1.5 \text{ kg } N_2O\text{-N ha}^{-1} \text{ year}^{-1}$ (see Figure 4-5a), showing examples of model failure to simulate N_2O peaks (A & B), failure to simulate the timing of N_2O peaks (B), and underestimation of N_2O peak magnitude (C).

5 EVALUATING DAYCENT MODEL PERFORMANCE ESTIMATING SOIL CARBON AND NITROUS OXIDE EMISSIONS IN SOUTH CENTRAL BRAZILIAN SUGARCANE PRODUCTION SYSTEMS⁴

5.1 Introduction

In the developing global bioenergy industry, Brazilian ethanol production from sugarcane (*Saccharum officinarum* L.) holds an important position due to its history as a dominant nationally-scaled biofuel, combined with its recognized potential to serve growing global demands for bioethanol (Goldemberg et al., 2014). Brazil has been a lead producer of fuel ethanol from sugarcane since the 1970's, with policies that supported large-scale national development and use (Solomon et al., 2007). In the most recent decade international export of Brazilian sugarcane has increased. This increase is driven in part by the high productivity of sugarcane combined with the relative ease with which it can be converted into ethanol, as well as in part by Brazilian efforts to export national expertise in ethanol production (Solomon et al., 2007; Wells and Faro, 2011). Growing international demand has consequently supported the expansion of land area devoted to sugarcane production in Brazil. This expansion is reflected in the construction of increasingly large sugarcane processing facilities. As of 2010, for example, 30 existing facilities could process over 3 Mt sugarcane per year while developing facilities were anticipated to process 3 – 4 Mt sugarcane per year, each of the latter requiring ~56,000 ha of land (Seabra et al., 2010). Between the years 2000 – 2012 land area for sugarcane production increased by nearly 5 Mha in Brazil, with half devoted to bioenergy production (Goldemberg et al., 2014; Mello et al., 2014).

The rapid, large-scale, and potentially continued expansion of sugarcane production in Brazil elicits several concerns for the sustainability of sugarcane-based bioenergy. Generally, sustainable crop-based biofuel development is expected to meet criteria for positive or minimal impact on soil fertility

⁴ In preparation for submission to BioEnergy Research with A. Silva, F.F.C Mello, C.E.P. Cerri, M.J. Easter, C. Davies, C.C. Cerri and K. Paustian.

and function, food production, soil C storage, soil greenhouse gas (GHG) flux, and ecosystem services (Reijnders, 2006). In developing global legislation, however, there is an emphasis on supporting biofuels with minimal greenhouse gas impacts ((Congressional Research Service, 2007), see also (Goldemberg et al., 2014)). Greenhouse gases accumulating in the atmosphere—largely from human sources—are warming the globe, causing impacts on human societies and natural systems which will continue to expand and be sustained for centuries (Collins et al., 2013; Forster, 2007). Fossil fuel combustion is a dominant source of these emissions, releasing carbon into the atmosphere that otherwise would have remained stored for geologically long periods of time. Thus bioenergy has the potential to reduce the GHG emissions by substituting for fossil fuels, but this requires understanding and effectively managing the fluxes from which greenhouse gases can be derived in the process of growing, processing, and using crop-based biofuels for energy (Cherubini, 2010). While greenhouse life cycle assessment methods address many aspects of biofuel production chains with increasing sophistication (Cherubini, 2010; Lee, 2004), the heterogeneity of ecosystem processes involved in determining the soil C and direct GHG fluxes impacts of bioenergy crop production remain a challenge.

In Brazilian sugarcane production there has been a recent focus on evaluating direct soil C impacts of land use conversion into sugarcane production (Mello et al., 2014). Land use change has been long recognized as an area for agriculture to act as a sink versus source of CO₂ (Paustian et al., 1998) and in bioenergy production is additionally recognized as holding long-term implications for the life cycle GHG emissions associated with crop-based bioenergy production (Searchinger et al., 2008). In Brazil there is particular concern with expanded sugarcane production pushing soybean production and cattle grazing, accompanied with deforestation, closer to the Amazon region (Wells and Faro, 2011), although legislation has been established to prevent the conversion of native lands into crop production (Goldemberg et al., 2014). Rather, there is greater focus on changing how existing agricultural and pasture lands are used, to accommodate the expansion of sustainable sugarcane production

(Goldemberg et al., 2014; Mello et al., 2014). These developments combine with a widespread shift from the tradition of burned sugarcane harvest to unburned and mechanized harvest—driven by legislation in the late-1990's and early 2000's—to make soil C a focal component of both experimental and modeling work in Brazilian sugarcane production systems (Galdos et al., 2009; Galdos et al., 2009a; Hassuani et al., 2005).

A missing component coming now under close scrutiny is the impact of sugarcane management practices on GHG emissions, with specific focus on changes in nitrous oxide (N₂O) emissions from burned versus mechanical harvest (de Oliveira Bordonal et al., 2012; Galdos et al., 2009), application of organic ethanol production byproducts such as vinasse and filtercake (Carmo et al., 2013; de Oliveira et al., 2013; Paredes et al., 2014), different levels of residue return following harvest (Carmo et al., 2013), and application of different forms of synthetic fertilizer (Signor et al., 2013). Other studies have used lower tier Intergovernmental Panel on Climate Change (IPCC) methods to determine the N₂O emissions from different Brazilian sugarcane production practices (De Figueiredo and La Scala Jr., 2011). However, direct measurements indicate a high level of variability in the emission of N₂O from nitrogen inputs during sugarcane production, relative to IPCC estimates (Carmo et al., 2013; de Oliveira et al., 2013; Signor et al., 2013). Process-based ecosystem models can integrate multiple land use changes and crop management practices, across varying soil and climate conditions, in order to estimate the soil C and GHG emission impacts of different types of bioenergy production systems (Campbell et al., 2014; Galdos et al., 2009; Muth and Bryden, 2013; Zhang et al., 2010). In order to evaluate the climate impact of sugarcane production practices at larger scales, there is a need to use such process-based models to integrate the interaction between land use change, sugarcane production practices, and spatially and temporally varying biophysical factors that drive the emission of GHGs from soils.

The DAYCENT ecosystem model has been used to simulate soil C and GHG emission impacts of bioenergy cropping systems (Campbell et al., 2014; Duval et al., 2013; Gao et al., 2013), while its

predecessor CENTURY has been used to successfully evaluate some of the different Brazilian sugarcane management practices listed above (Galdos et al., 2009). The DAYCENT model was used to evaluate the GHG impacts of land use conversion from pasture into energy cane in Florida, USA (Duval et al., 2013). In this analysis we use data from a collection of studies in South Central Brazil to parameterize and validate DAYCENT model performance simulating sugarcane production and soil C. One of the challenges in Brazil is the relative paucity of high quality weather stations and meteorological data over large areas of the country, since weather variables (temperature and precipitation) are important drivers for soil N₂O fluxes. Thus we evaluated DAYCENT estimation of N₂O emissions and compare modeled versus measured estimates of N₂O emission factors using two different sources of climate data: 1) nearest meteorological station data and 2) interpolated weather data from the Climate Forecast System Reanalysis (CFSR) global meteorological dataset (Fuka et al., 2014). DAYCENT simulations are highly limited by the quality, availability, and continuity of available weather data. A standardized resource like CFSR can be invaluable to drive DAYCENT simulations over larger areas. The comparison of weather data estimations in this analysis aims to contribute towards the use of DAYCENT for larger-scale regional and national analyses of GHG emissions with sugarcane production practices in Brazil.

5.2 Materials and Methods

5.2.1 Experimental Data

To parameterize the DAYCENT model, data were collected from a selection of published studies grouped in the South Central region of Brazil (Figure 5-1). Most studies measured a single type of data, specifically soil C, N₂O emissions, or aboveground production. Therefore the parameterization studies were selected to represent data gathered from experiments that included the main management practices of interest from the perspective of N₂O emissions, including mineral fertilizer application, vinasse application, residue return, and burned versus unburned harvest (Table 5-1). Parameterizing DAYCENT to accommodate this range of management practices, across yields, soil C, and N₂O emissions

may therefore result in a more general model performance for estimating GHG impacts with management practices over a broader area.

Measured data were converted into units comparable to DAYCENT model results, expressed in units of g C m^{-2} for sugarcane production, $\text{g N}_2\text{O-N ha}^{-1} \text{ yr}^{-1}$ (or day^{-1} , or cumulative over the 15- and 50-day experiments) for nitrous oxide flux, and g C m^{-2} from 0 – 20cm for soil organic matter. Aboveground production and stalk yields were reported as either weight at harvest, dry weight, or C mass per unit area (Table 5-1). Sugarcane stalks have a percent moisture that can exceed 80% during peak growth, with an ideal range for sugarcane harvest between 70-74% (Bakker, 2012). No moisture contents were directly reported in studies with data on stalk harvest weights. If stalk measurements were not reported in terms of C mass per unit area, the measurements were assumed to contain 70% water and 45% C content, using these values to convert harvest or dry weight into g C m^{-2} . This approach is similar to that used by Galdos et al., (2009) in a CENTURY model study of sugarcane production, but may overestimate stalk C if 70% water is lower than the true water content at harvest.

Soil C data from Mello et al. (2014) consist of a large set of paired field comparison sites (under different land uses), which included all sites where sufficient data were available for DAYCENT model simulations. We were able to include 63 of the original 135 study sites, as well as 28 of the original 75 conversion pairs, across eight regions (Table 5-1). This subset of sites predominantly represents areas of pasture conversion into sugarcane, although one region included conversion of two native vegetation sites into sugarcane while another included three sites with conversion of agricultural lands into sugarcane (Table 5-1). The eight regions are geographically spaced across the longitudinal gradient of the main South Central sugarcane producing region in Brazil (Figure 5-1). This study also provides the only dataset where sufficient data were available to split their use between DAYCENT parameterization versus out-of-sample validation of DAYCENT performance. We therefore divided these sites into two groups, using one group of sites across four regions (Itirapina, Ipaussu, Igarapava, and Gioiatuba) for soil

C parameterization while reserving those located in the other four regions (Anhembi, Arapora, Maracaju, and Iacanga) for soil C validation. We split these sites randomly across the longitudinal extent of the South Central region, such that parameterization and validation sites were located across comparable longitudinal reach (Figure 5-1). Insufficient sites were available to extend parameterization versus validation sites across comparable latitudinal area. The sites in the regions reserved for DAYCENT validation included >70% of all of the Mello et al. (2014) sites simulated in this analysis, or 46 of the 63 total.

To evaluate N₂O emissions we used three studies with direct measurement of N₂O emissions in four locations, representing 27 different experimental treatments that included burned versus unburned harvest, application of vinasse, varying levels and forms of synthetic fertilizer addition, and different amounts of residue return following harvest (Table 5-2). Exact experimental start dates were variably reported; Carmo et al. (2013) reported the experimental start day for one location (Piracicaba), while only reporting the starting month for the other location (Jaú). Signor et al. (2013) reported the exact start date, while Oliveira et al. (2013) indicated only that the experiment started in July and continued into August. When not reported, we used estimated values to schedule the days of experimental events in DAYCENT simulations. In all studies, N₂O emissions measured using static polyvinyl chloride chambers had between 3 and 5 replicate chambers per treatment.

5.2.2 DAYCENT model overview

The DAYCENT model runs on a daily time-step and simulates soil processes by horizon across the soil profile, including soil nutrient movement, water movement, plant growth, and many other ecosystem components (Del Grosso et al., 2008). The key drivers of DAYCENT include maximum and minimum daily temperature, daily precipitation, soil texture, and land management (including specific plant types grown and soil management such as tillage and nutrient additions). Nitrous oxide emissions are derived from nitrification and denitrification, based on soil water content and soil texture, NH₄⁺ and

NO_3^- concentration, and availability of labile C as estimated using heterotrophic respiration as a proxy (Parton et al., 2001). Nitrate is mobile and can be either leached or taken up by plants. It is therefore controlled by interactions with either plants or water movement across the soil profile. Ammonium is immobile and only distributed in the top 15cm of the soil profile. On a daily time step, denitrification is determined by soil texture, water content, temperature, NO_3^- availability, and heterotrophic respiration, while nitrification is determined by the same soil factors (texture, water content, temperature) alongside NH_4^+ concentration only in the 0 – 15cm layer (Del Grosso et al., 2008). The DDcentEVI version of DAYCENT (a version of DAYCENT with the option to use Enhanced Vegetation Index- i.e. EVI- data) was used for this analysis. DDcentEVI was developed and tested to estimate total agricultural land use emissions for the US Environmental Protection Agency's (EPA) GHG emission inventory annual report (U.S. Environmental Protection Agency, 2013).

Temperature and precipitation are key drivers of biogeochemical processes, and are particularly important in the simulation of N_2O emissions. Long-term, continuous daily climate datasets are therefore needed to both represent regional climate patterns in spin-up simulations—i.e. that bring DAYCENT to equilibrium conditions prior to simulating experimental treatments—as well as to drive simulations for the experimental periods of interest. As mentioned above, in this study we considered two climate datasets for simulating N_2O flux from experimental treatments, in addition to directly reported climate data. The first climate dataset consisted of climate data drawn from the nearest available meteorological station to each study location, provided by the *Agrometeorological Monitoring System* (AGRITEMPO). These data ranged in their temporal span, starting as early as 1917 and as late as 2007, and extending mainly to 2010 although in the Maracaju region data were available until 2011. Our second climate data source was the Climate Forecast System Reanalysis (CFSR) global meteorological dataset (Fuka et al., 2014), which is accessed using the EcoHydRology R package. These climate data are generated using site-specific latitude and longitude, and are given at a 38-km scale from 1979 – 2013

using algorithms to interpolate weather for areas between weather stations. The CFSR dataset is under active evaluation and is considered, in the tropics, comparable to a quality weather station at a 30 – 40km distance from the experimental location (D. Fuka, personal communication). These climate datasets vary considerably from each other and from climate data reported in the studies considered in this analysis, in terms of temperature biases, the timing, magnitude, and cumulative amount of precipitation, as well as in the prevalence of missing data. A summary of reported climate versus the two climate datasets used to drive DAYCENT simulations in this analysis are reported in Table 5-2.

Soil texture and prior land use history used for model initialization were drawn, where available, from data reported in the publications included in this study, as well as from additional publications presenting different datasets from the same experimental sites. For the Mello et al. (2014) land conversion sites, additional land use history and sugarcane production practices data were acquired directly from managers of nearby sugarcane processing facilities. In addition to the 63 land use conversion sites from Mello et al. (2014), 42 different sugarcane management practices were simulated matching experimental management practices in the 6 studies that provided the sugarcane production and N₂O emission measurements used in this study (Table 5-1).

5.2.3 Climate data modifications for simulating N₂O emissions

In order to evaluate the accuracy with which the two climate datasets described above reflect environmental conditions driving N₂O emissions, in this analysis we chose to focus on reported versus climate dataset estimations of precipitation. Specifically, in our analysis we compared measured versus DAYCENT modeled N₂O emissions for all treatments as estimated using unaltered version of each climate dataset, and as estimated using as many directly reported precipitation data as were available for each experimental site. Only mean annual climate data were reported in Carmo et al. (2013) (Table 5-2). Therefore we simulated these treatments using only each of the two climate datasets, without alteration. In Signor et al. (2013), daily precipitation data were reported for the 50-day experimental

period. Therefore these treatments were simulated using each of the two climate datasets, without alteration, as well as simulated using each of the climate datasets with the reported precipitation data integrated in place of the original values. In the 15-day Oliveira et al (2013) study only monthly summaries of climate data were reported for the year in which the experiment took place (Figure 5-7). However, water-filled pore space was reported for the 15-day experimental period. The water-filled pore space data indicated a likely precipitation event early in the experimental period not reflected in either of the two climate datasets, while the reported monthly summaries of precipitation data show that each of the climate datasets were substantially underestimating precipitation during the experimental period (Figure 5-7). Therefore the treatments in Oliveira et al. (2013) were simulated using each of the two climate datasets, without alteration, as well as using each of the two climate datasets where the estimated 'missing' precipitation was added, evenly divided on a daily basis for the month preceding the experimental period.

5.2.4 Statistical Analyses

Statistical analyses were written in R-3.1.1 software (R Core Team, 2014), using tidyr (Wickham, 2014), dplyr (Wickham and Francois, 2015), hydroGOF (Zambrano-Bigiarini, 2014), and ggplot2 packages (Wickham, 2009). Regression analyses were used to compare measured versus modeled total C in aboveground sugarcane production (g C m^{-2}), C in sugarcane stalk production (g C m^{-2}), total soil C (g C m^{-2}), and the difference in soil C between paired Mello et al. (2014) land use conversion sites (g C m^{-2}). Regression analyses were additionally used to compare measured versus modeled cumulative and daily N_2O flux ($\text{g N}_2\text{O-N ha}^{-1} \text{yr}^{-1}/\text{day}^{-1}/15\text{-day}^{-1}/50\text{-day}^{-1}$) across all sites where these data were available. Root mean square errors were calculated for all comparisons, to evaluate relative model performance across different types of measured observations. A two-tailed test was used to compare measured versus modeled validation soil C results by region, calculating 95% confidence intervals (mean +/- the

standard error * 1.96), where overlap between confidence intervals indicates no statistical difference between means.

5.3 Results

Primary productivity and soil C are a primary focus for evaluating baseline DAYCENT performance; in either case in this analysis, DAYCENT was able to capture trends in treatment effects on sugarcane yields and soil, but with high variability. For example, after parameterization, DAYCENT simulated total aboveground sugarcane production with minimal bias but high dispersion, with a slope close to 1 and an intercept that did not differ significantly from 0, but a low adjusted r^2 of 0.3 (Figure 5-2, A). Stalk production had higher dispersion (a lower adjusted r^2) and more bias, with a slope less than 1 and an intercept that significantly differed from 0 (Figure 5-2, B). However stalk yield data were more uncertain due to unreported percent water content at harvest. Therefore, we have greater confidence in the quality of the total aboveground measured data in evaluating DAYCENT performance (Figure 5-2, A). Predicted C:N ratios of the sugarcane trash were consistent with reported values, ranging from 79-100 (data not shown), which are very similar to the 80 – 100 C:N ratio reported in published literature (Gava et al., 2005). DAYCENT may therefore be variable in how accurately it simulates the quantity of litter input that it simulates for sugarcane, but DAYCENT is relatively consistent in simulating the litter's C:N ratio.

DAYCENT did reflect overall trends in soil C in most regions simulated in this analysis, but given the high variability of the measured soil C data it is difficult to be conclusive in the valuation of overall DAYCENT performance for soil C dynamics. After parameterization, model predictions of total soil C showed a significant relationship, with a higher r^2 than production predictions (Figure 5-2), and an intercept that did not differ significantly from 0. However, model predictions showed a tendency to overestimate low soil C values while underestimating high soil C values, as indicated by having a slope <1 (Figure 5-3). The set of regions from Mello et al. (2014) used to validate the DAYCENT model showed

variable model performance by region. In simulating total soil C and the difference between paired LUC sites included in Mello et al (2015), model performance was more comparable to measured values in Arapora and Anhembi, performed more poorly estimating total soil C in Iacanga, and did not accurately estimate either total soil C or the difference in soil C between paired sites in Maracaju (Figure 5-4).

DAYCENT simulations of N₂O emissions were highly sensitive to precipitation data inputs. Precipitation data from the two climate datasets considered in this study were, in turn, variable relative to reported precipitation information. In estimating annual N₂O emissions for the two sites in the Carmo et al. (2013) study, DAYCENT performance was improved using the nearest weather station versus the interpolated dataset (Figure 5-5, A), but with both analyses showing a tendency to overestimate annual N₂O emissions (intercept significantly greater than 0) that was more pronounced with the interpolated climate dataset (Figure 5-5, A). In Carmo et al. (2013) the only reported climate data were annual averages (Table 5-2). It is therefore difficult to assess this site's model performance and sensitivity related to precipitation data on a finer timescale. The model estimation of annual emissions in Carmo et al. (2013) using the nearest weather station climate dataset provided the best estimate of treatment effects on relative N₂O emissions, with a slope closest to 1 of all cumulative modeled/measured comparison (Figure 5-5). The overestimation of annual emissions using interpolated climate data was likely impacted by a bias towards high annual precipitation in the dataset for this location (Table 5-2). Cumulative measured versus modeled comparisons for the shorter-term experiments (50 days for Signor et al. (2013) (Figure 5-5 & 5-6), 15 days for Oliveira et al. (2013)) showed poorer DAYCENT simulation of treatment effects, with the latter having no significant relationships between measured and modeled values using either climate dataset.

In Signor et al. (2013), precipitation measurements for the experimental period were directly reported; however, these precipitation data did not improve cumulative model performance when incorporated into the climate datasets used to drive model simulations (Figure 5-6, A & B). These results

suggest the precipitation *preceding* the experimental period is important for accurately capturing N₂O emissions *during* the experimental period; model performance was improved using reported precipitation in the interpolated climate dataset, which has higher overall precipitation (Figure 5-5 & 5-6, B).

However, on a daily basis direct precipitation measurements did support more accurate N₂O emission estimates in some treatments from Signor et al. (2013). Using the interpolated dataset and reported precipitation, DAYCENT performed well with both the timing and magnitude of daily N₂O emissions in Signor et al., when N additions and measured N₂O emissions were low (Figure 5-6, C). However these model simulations increasingly diverge as N additions and measured N₂O emissions increased (Figure 5-6, A & B, D). The treatment with extremely high measured N₂O emissions (180 kg N ha⁻¹ ammonium nitrate) was excluded from these measured/modeled comparisons (Figure 5-6, A & B), to better evaluate the range of treatments where DAYCENT currently shows greater success. DAYCENT performance for the specific 180 kg N ha⁻¹ ammonium nitrate treatment was universally poor, indicating factors that result in exceptionally high emissions in sugarcane systems are not represented well in DAYCENT.

Oliveira et al. (2013) cumulative simulated emissions were 1 – 2 orders of magnitude less than reported measurements, with no significant relationship between cumulative measured versus modeled values using either of the two climate datasets. This indicates very poor model performance at this site. However, while summary climate data would suggest these climate datasets are estimating excessively high precipitation on an annual basis for Oliveira et al. (2013) (Table 5-2), a comparison of monthly reported versus estimated precipitation reveals a bias towards very low precipitation estimates in both climate datasets during the experimental period (7.2 cm in July reported, versus 1.8cm from the nearest weather station and 2.4cm from the interpolated climate dataset, Figure 5-7). When the difference in precipitation was added on an even daily basis in the month preceding the experimental period, model

performance for daily emissions in the burned treatments improved substantially, although showing more sensitivity to water additions than to N addition with vinasse (Figure 5-8). Model simulations of mechanical harvest treatments were also improved in these simulations but still an order of magnitude too low relative to measured values (data not shown). Therefore there are structural improvements needed for DAYCENT to better simulate the impact on N₂O emissions of high litter inputs added back to the soil with mechanical harvest. The exact experimental start date was not reported in Oliveira et al. (2013). Model variability based on available climate data versus the need for structural model improvements would be better clarified by lining up the precipitation data and the experimental period more exactly, particularly with such a short-term experiment.

Modeled estimates of N₂O emission factors—the percentage of N₂O-N released per unit of N applied to the soil—showed high variability, due to both variability in climate data accuracy as well as the need for improved model simulation of very high N₂O emission periods and locations. Only the original climate datasets were used in this analysis of EFs. Model EFs ranged from greater than 5% to less than 0.1%. This range therefore extends an order of magnitude lower and at least 5x higher than the IPCC emission factor (Figure 5-9). This variability was comparable to measured variability that exhibited a similar high range, but with a lowest value of only 0.31%. Regardless of climate data source, the highest measured EF was not successfully predicted by model simulations. The tendency of N₂O overprediction in the Piracicaba site in Carmo et al. (2013), in turn, resulted in extremely high predicted emission factors.

5.4 Discussion

In this analysis, the DAYCENT model was parameterized using measured data for sugarcane aboveground production, soil C and N₂O emissions drawn from publications that represented a range of management practices and land use conversions of key concern in determining the sustainability of Brazilian sugarcane production. The results from the validation component of this study, evaluating

DAYCENT performance simulating soil C, demonstrate that the DAYCENT model is capable of simulating soil C trends under different land conversion scenarios, but with variable regional performance. The poorest performance in the validation component of this study was in the simulation of sites in the Maracaju region. However Maracaju differs from the all other sites used in parameterization in two respects. First, Maracaju is situated furthest west and is geographically distanced from all other sites (Figure 5-1). Second, sites in the Maracaju region include only land use conversion from active agricultural production into sugarcane. The sites used for parameterization in this study did not include any conversion of agricultural production into sugarcane. Poor DAYCENT performance simulating Maracaju sites indicates a need to expand DAYCENT parameterization into both this region as well as into the evaluation of agricultural land conversion into sugarcane production. This would allow for DAYCENT use simulating land conversion of key concern in the development of Brazilian sugarcane (Carvalho et al., 2009; de Souza Braz et al., 2013; Mello et al., 2014).

With the exception of Maracaju, model results generally matched the direction and variability of mean regional measured values of differences in soil C between paired land use conversion sites (Figure 5-4, B). As discussed above, the sites in these remaining regions predominantly represent pasture conversion into sugarcane. Conversion from pasture into sugarcane was shown in Mello et al. (2014) to result in a cumulative soil C loss, a trend reflected in measured means in these regions (Figure 5-4, B). Our modeled results support that trend, but with high variability. By necessity the number of paired sites in this DAYCENT validation study was substantially reduced from those included in the original analysis, due to limited data available to drive DAYCENT simulations. Studies show that it is possible for productive soils to store more C than native Cerrado (Carvalho et al., 2009), particularly with high C storage under pasture (Figueiredo et al., 2013) and grasslands due to root contributions (Fidelis et al., 2013). Results shown in Figure 5-4 do reflect the trend of higher C storage in pasture versus sugarcane production. However a greater diversity of soil C measured data are needed to explore other aspects of

soil C change with land management practices, and further evaluate this aspect of DAYCENT model performance.

Model parameterization and validation focused on aboveground sugarcane production and soil C were mainly intended to ensure a sufficient level of basic DAYCENT performance simulating key ecosystem properties. These values are considered benchmarks in the evaluation of land-surface models (Luo et al., 2012), and are similarly a primary concern in assessing baseline DAYCENT performance. In the simulation of N₂O emissions from sugarcane production management practices, the selection of studies included in this analysis represent the main management practices of concern for impacts on N₂O emissions—i.e. residue management, mineral fertilizer application, organic fertilizer application, and harvest methods. However, we had insufficient replications of treatments across sites to consider general rather than site-specific estimations of N₂O emissions with specific management practices. Therefore, we considered model performance in aggregate across management practices, which further demonstrate the challenge of modeling the extreme temporal and spatial heterogeneity of N₂O emissions in sugarcane production systems.

In this analysis, evaluating DAYCENT simulation of N₂O emissions was limited by the short 15- and 50-day length of the Signor et al. (2013) and Oliveira et al. (2013) experiments, in addition to the variable supplemental data on experimental start dates and precipitation that these studies provided. While these types of short-term measurement periods are valuable in evaluating model performance simulating GHG emissions for specific types of management practice events, model performance will likely diverge from measured values on a daily basis if the timing of experimental treatments is estimated rather than informed directly. For example, model simulations are less likely to estimate the exact timing or the extremes of N₂O emissions, if estimated days for experimental treatments do not line up with the environmental conditions when the measurements were taken—e.g. if simulated fertilizer application occurs in a dry series of days, when in reality it occurred in close proximity to a

large rain event. Additional short-term studies would be useful for further evaluating N₂O emissions from sugarcane management practices of interest, and support DAYCENT estimations for the GHG impacts of specific management practices on a more regional basis. However, longer-term N₂O emission measurement time series are also needed, to better determine the time scale at which DAYCENT can most accurately estimate N₂O flux from sugarcane production.

Despite their limitations, the data used in this analysis do give widespread support to the importance of using high quality, long-term climate data to drive the evaluation of N₂O emissions from Brazilian sugarcane production practices using DAYCENT. In this analysis we experimented with different forms and combinations of weather data, using the two climate datasets in addition to reported climate information. The results suggest that climate data need to accurately reflect conditions before and during experimental treatments being evaluated, in order to more closely approximate the N₂O emission dynamics that occur from specific types of sugarcane management practices. This again addresses the need, mentioned above, for longer-term N₂O measured datasets. In other studies DAYCENT performance tends to improve when evaluating N₂O emissions over longer temporal periods: the model may not accurately capture specific daily emission events, particularly if the driving climate data do not reflect true climate conditions. However, DAYCENT tends to compensate over longer time-spans, again as long as the driving climate data reflect true conditions over the long term. Poor climate data—for example simulating inaccurately dry conditions or excessive precipitation when N sources are applied, as seen in this analysis—can substantially over- or under-estimate N₂O flux, sometimes even when a period of directly measured climate data are incorporated (Figure 5-6, A & B).

While climate data variability was responsible for some poor DAYCENT performance simulating N₂O flux in this study, DAYCENT also showed an inability to simulate the sometimes extremely high N₂O emissions than can occur in Brazilian sugarcane systems. In another study (Campbell et al., 2014), DAYCENT tended to perform more poorly simulating high levels of N₂O emissions (Figure 5-5 B),

particularly at a daily level (Figure 5-8). In this study the measured data (i.e. from Signor et al. (2013)) show the potential for conditions to occur in sugarcane that can release very high emission, that were subsequently missed by sometimes several orders of magnitude in DAYCENT. Similar conditions have been observed in Australian sugarcane systems, and are currently undergoing evaluation using DAYCENT (W. Parton, *personal communication*). Although these high emission events may be rare and short-term, they can be a substantial contributor to total N₂O emissions. One aspect of DAYCENT performance that may be contributing to these patterns of underestimation is DAYCENT's lack of explicit dissolved organic carbon simulation, which could transport some of the very large amounts of surface litter inputs following mechanical harvest in a form and a direction that would support higher denitrification in the soil. However, DAYCENT does not yet simulate the movement of DOC across the soil profile, although this feature is currently in development (Campbell et al., in preparation for Soil Biology and Biochemistry). The lack of sensitivity of the mechanically harvested treatments in Oliveira et al. (2013) to additional precipitation, as compared to the burned harvested treatments, supports that a limiting factor related to litter inputs is likely contributing to poor DAYCENT N₂O emission simulation of those treatments.

Our results further demonstrate the challenge of simulating the extreme variability in emissions factors for N₂O. Certainly the standard Tier 1 IPCC value may not reflect true N₂O emissions from a given location or sugarcane management practice. However, while DAYCENT modeling would support a Tier 2 IPCC approach to GHG evaluation, the large discrepancy between modeled versus measured evaluation of high N₂O emissions must first be addressed, and a robust climate dataset to drive regional DAYCENT simulations either identified or developed.

Table 5-1 Site descriptions.

Study	Collection Period	Data description	Lat/Long	Texture	Description
N₂O Emissions					
(Carmo et al., 2013)- Piracicaba	335 days, on event basis	Est. daily & annual flux, from replicated static polyvinyl chloride chambers	-22.68/ -47.55	Sandy Clay Loam	Sugarcane production from 1990, unburned harvest, 0, 7, 14, 21 Mg/ha trash w vinasse
(Carmo et al., 2013)- Jaú	314 days, on event basis	Est. daily & annual flux, from replicated static polyvinyl chloride chambers	-22.25/ -48.57	Sandy Loam	Sugarcane production since 1990, unburned harvest, mineral fertilizer & vinasse
(Signor et al., 2013)- Piracicaba	50 days, every 1-2 days	Est. daily & cumulative flux, from replicated static polyvinyl chloride chambers	-22.72/ -47.63	Clay	Urea and ammonium nitrate fertilizer applications
(de Oliveira Bordonal et al., 2012)- Boa Vista Farm Piracicaba	15 days, every 1-2 days	Est. daily & cumulative flux, from replicated static polyvinyl chloride chambers	-18.72/ -46.97	Clay	Burned vs unburned, vinasse vs water
Sugarcane Production					
(Franco et al., 2010)- Pirassununga	Plant cane harvest (1 yr)	Dry matter (kg ha ⁻¹): total, stalk	-21.92/ -47.17	Clay	Different rates of urea applied to crops at planting
(Franco et al., 2010; Otto et al., 2009)- Jaboticabal	Plant cane harvest (1 yr)	Dry matter (kg ha ⁻¹): total, stalk	-21.32/ -48.32	Sandy Clay Loam	Different rates of urea applied to crops at planting
(Hassuani et al., 2005)- Usina São Martinho	Plant cane harvest + 5 ratoons (6 yrs)	Harvest weight (t ha ⁻¹): aboveground total, trash	-22.36/ -47.38	Sandy Clay Loam	unburned harvest with 0, 33%, 66%, and 100% trash
(Hassuani et al., 2005)- Usina Santa Luisa	Plant cane harvest + 1 ratoon (2 yrs)	Harvest weight (kg plot ⁻¹): aboveground total, stalk, trash	-22.58/ -47.52	Clay	unburned harvest of sugarcane
(M V Galdos et al., 2009)- Usina São Martinho	Plant cane harvest + 7 ratoons (8 yrs)	Stalk C (g m ⁻²), assuming 70% water content & 44% C content from fresh weight	-21.37/ -48.05	Clay	burned vs unburned sugarcane
Soil Carbon					
(Mello et al., 2014)- Igarapava	Sampled with replicates, 2010	Soil C (%) by 10cm layer from 0 – 100cm	-20.16/ -47.77	Clay	7 sites: sugarcane/pasture conversion, 2 conversion pairs (parameterization)
(Mello et al., 2014)- Ipaussu	Sampled with replicates, 2010	Soil C (%) by 10cm layer from 0 – 100cm	-23.11/ -49.52	Clay	5 sites: sugarcane/pasture conversion, 3 conversion pairs (parameterization)
(Mello et al., 2014)- Itirapina	Sampled with replicates, 2010	Soil C (%) by 10cm layer from 0 – 100cm	-22.37/ -47.91	Loamy Sand	4 sites: sugarcane/pasture, 3 conversion pairs (parameterization)
(Mello et al., 2014)- Gioiatuba	Sampled with replicates, 2010	Soil C (%) by 10cm layer from 0 – 100cm	-18.09/ -49.62	clay loam	1 sugarcane/pasture conversion site (parameterization)
(Mello et al., 2014)- Anhembi	Sampled with replicates, 2010	Soil C (%) by 10cm layer from 0 – 100cm	-22.75/ -48.02	Loamy Sand	11 sites: sugarcane/pasture conversion, 4 conversion pairs (validation)
(Mello et al., 2014)- Arapora	Sampled with replicates, 2010	Soil C (%) by 10cm layer from 0 – 100cm	-18.47/ -49.12	Clay	25 sites: sugarcane/pasture/native conversion, 13 conversion pairs (validation)
(Mello et al., 2014)- Iacanga	Sampled with replicates, 2010	Soil C (%) by 10cm layer from 0 – 100cm	-21.97/ -49.04	Loamy Sand	4 sites: sugarcane/pasture conversion, 3 conversion pairs (validation)
(Mello et al., 2014)- Maracaju	Sampled with replicates, 2010	Soil C (%) by 10cm layer from 0 – 100cm	-21.43/ -55.35	Clay	6 sites: agriculture/sugarcane conversion, 3 conversion pairs (validation)

Table 5-2 Summary climate data for the four sites with N₂O emission data, as reported and as calculated from weather data given by the nearest weather station versus the interpolated dataset from the Climate Forecast System Reanalysis global meteorological dataset .

Site	Reported Climate		Nearest Weather Station			Interpolated	
	Mean Annual Precip. (cm)	Mean Temp (°C)	Mean Annual Precip. (cm)	Mean Temp (°C)	Missing data (days/total)	Mean Annual Precip. (cm)	Mean Temp (°C)
Carmo- Piracicaba	139	21	132.7	22.7	91/2922	178	22.1
Carmo- Jaú	139	21	129.9	24.2	312/2557	133.9	23
Signor- Piracicaba	127	21.5	130.9	22.5	101/4383	170.8	22.2
Oliveira- Piracicaba	141.9	NR	122.2	23.3	13/3287	166.9	21.9

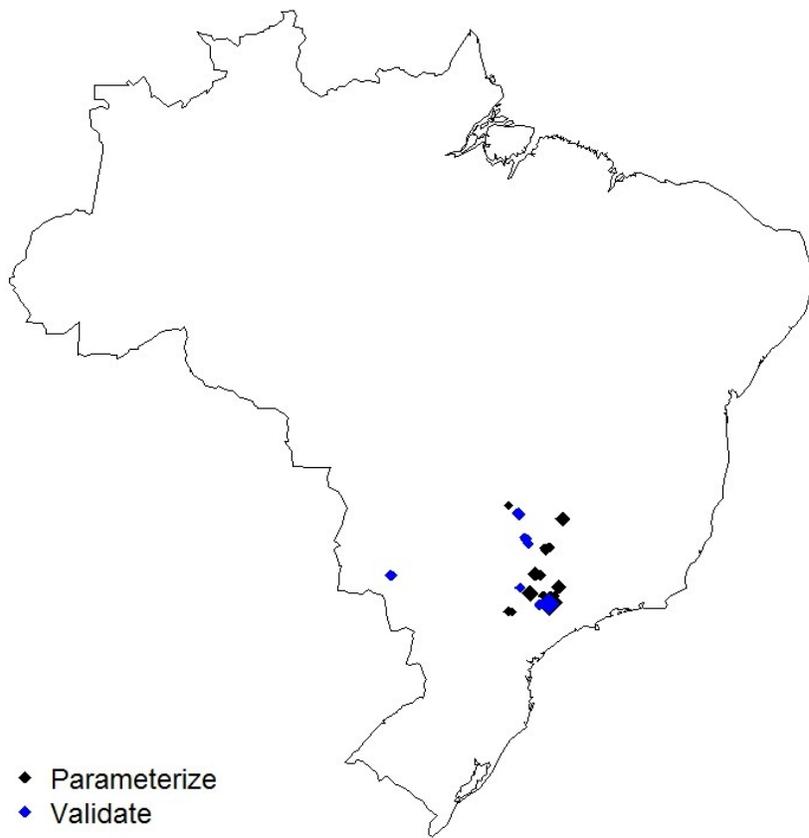


Figure 5-1 Location of sites used to parameterize and validate the DAYCENT model. Validation sites were selected to represent similar longitudinal gradients as sites used to parameterize the model.

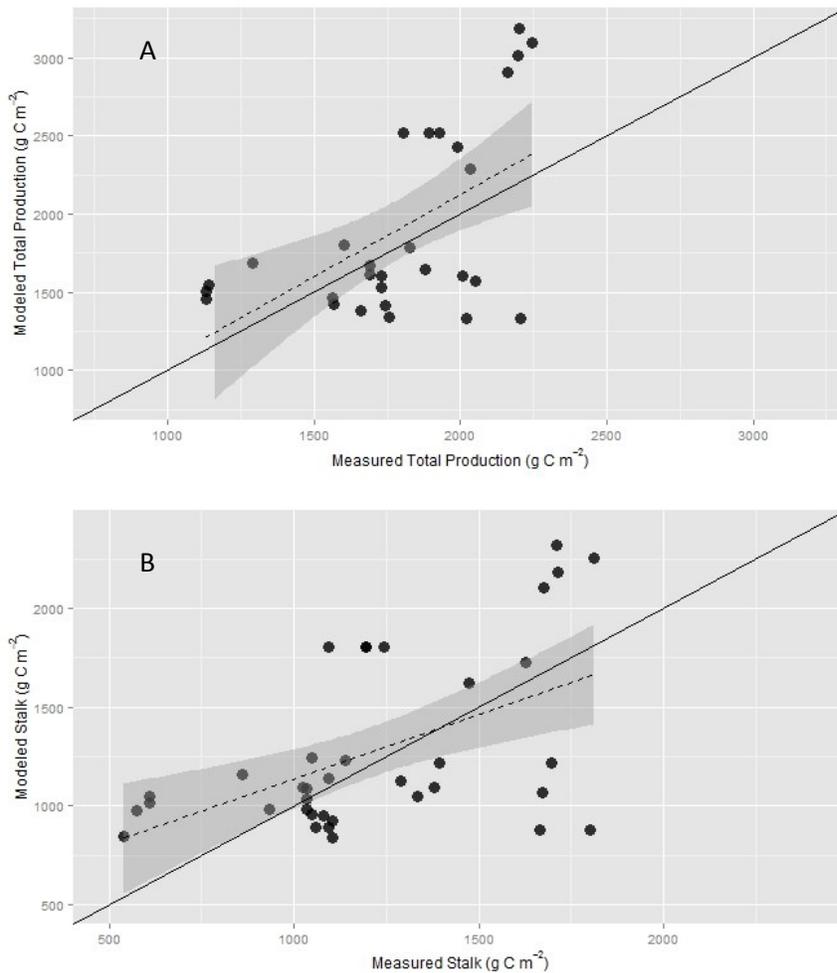


Figure 5-2 Within-sample measured (x-axes) versus modeled (y-axes) total aboveground production (A) and stalk production (B), both showing significant relationships (adjusted $r^2=0.3$, slope=1.05, $p=0.001$, RMSE=497 and adjusted $r^2=0.25$, slope=0.65, $p<0.001$, RMSE=396, respectively). However, while the total production had an insignificant intercept (intercept=25), the stalk production intercept was weakly significant (intercept=487, $p=0.04$). The 1:1 relationships are shown with the solid line, while linear regression relationships are shown with the dotted lines and shading.

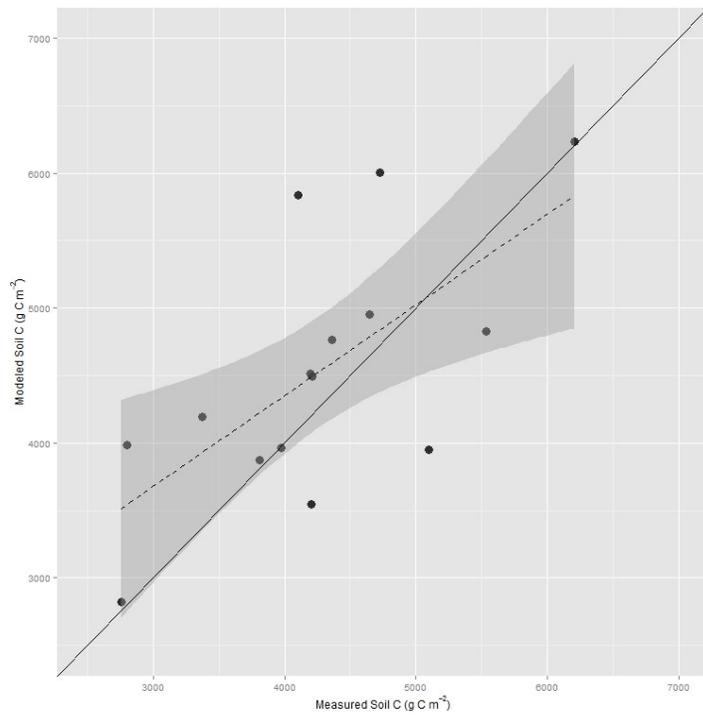


Figure 5-3 Within-sample measured (x-axes) versus modeled (y-axes) total soil C, showing a significant relationship and insignificant intercept (adjusted $r^2=0.4$, slope=0.67, $p=0.008$, RMSE=791; intercept=1660). The 1:1 relationship is shown with the solid line, while the linear regression relationship is shown with the dotted lines and shading.

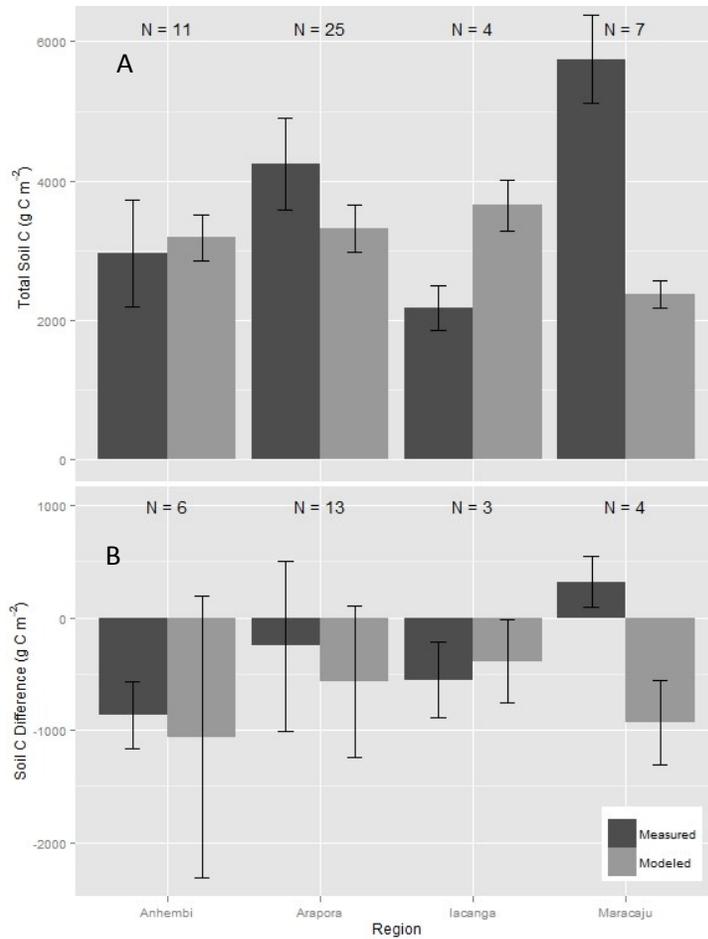


Figure 5-4 Out-of-sample measured versus modeled prediction of total soil carbon (A) and the difference in soil carbon between paired land use change sites from Mello et al. (2014) (B), for DAYCENT validation, showing 95% confidence intervals as well as the number of sites included in these analyses in each region. In A & B, Maracaju modeled and measured confidence intervals did not overlap. Iacanga total soil C modeled results were substantially higher than measured values (A), but soil C difference confidence intervals for the 3 sites with LUC pairs did overlap (B). Modeled and measured confidence intervals for Anhembi and Arapora overlapped in total (A) as well as by difference in paired sites (B).

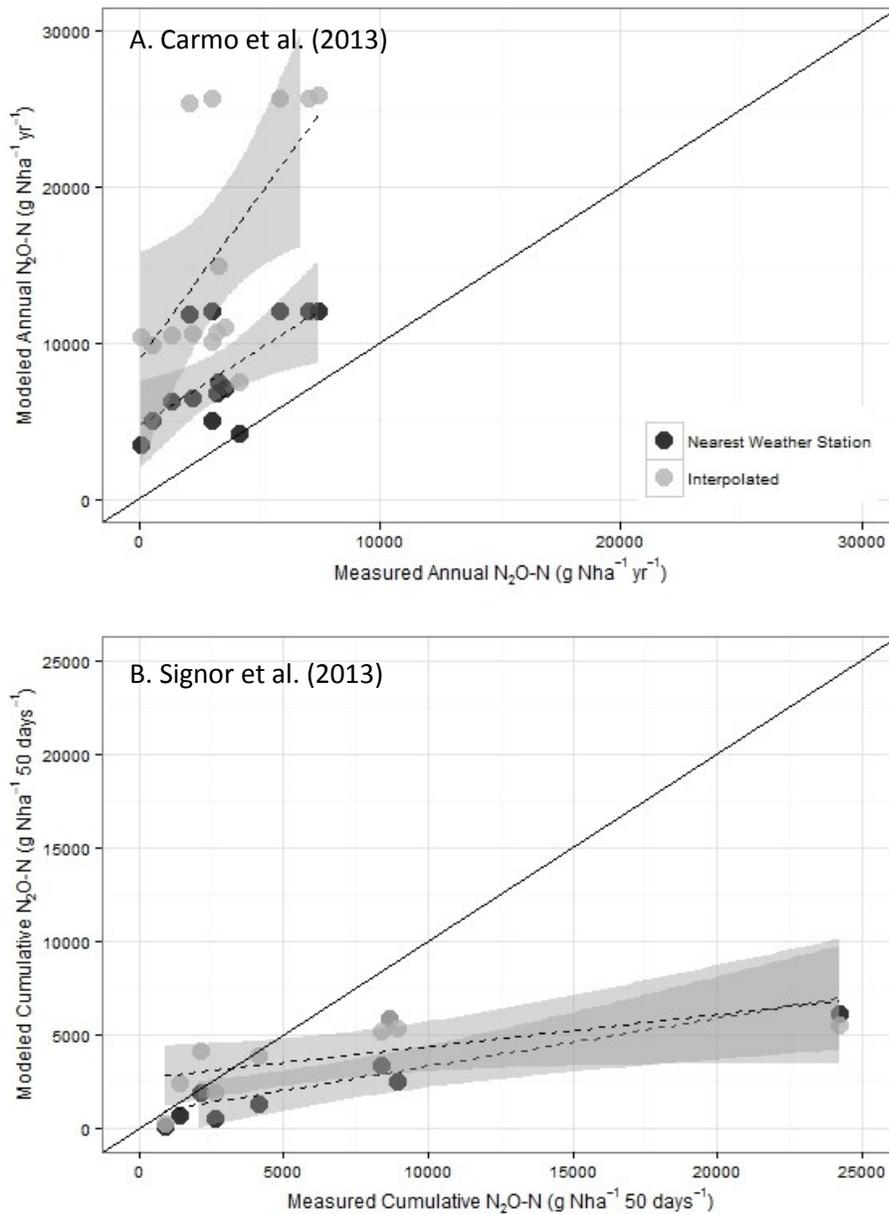


Figure 5-5 Measured (x-axis) versus modeled (y-axis) predictions of cumulative N_2O emissions for both sites in the long-term study by Carmo et al. (2013) (A) versus the Piracicaba sites in the 50-day study by Signor et al. (2013) (B), using nearest weather station versus interpolated climate data. Both types of climate data resulted in significant relationships between measured and modeled values in the Carmo et al. (2013) study (adjusted $r^2=0.38$, slope=0.98, $p=0.011$, RMSE=4700; and adjusted $r^2=0.32$, slope=2.1, $p=0.021$, RMSE= 14000, A), but intercepts that were significantly different than 0 (intercept=4799, $p=0.0036$; intercept=8900, $p=0.015$, A). In the Signor et al. (2013) study the nearest weather station data resulted in a significant relationship (adjusted $r^2=0.66$, slope=0.26, $p=0.0047$, RMSE=6771) and an intercept that was not significantly difference from 0 (intercept = 762, B). However, the interpolated climate data did not result in a significant relationship between measured values and modeled prediction. The 1:1 relationships are shown with the solid line, while linear regression relationships are shown with the dotted lines and shading.

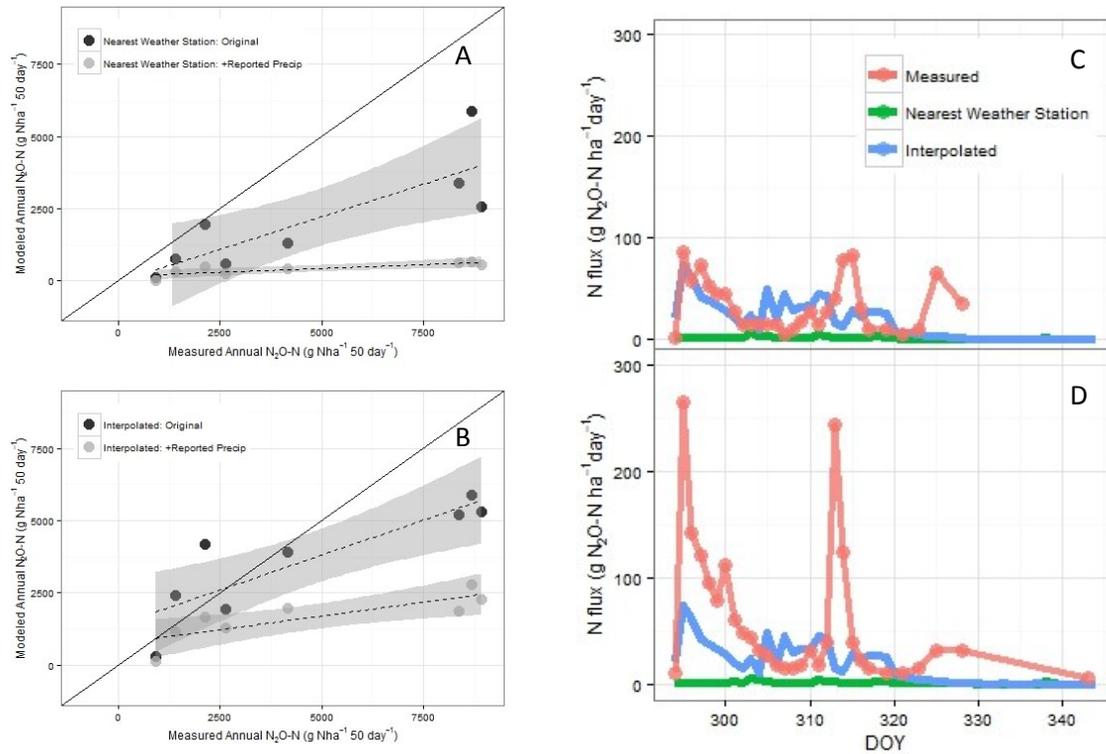


Figure 5-6 Measured (x-axis) versus modeled (y-axis) predictions, excluding the 180 kg $N ha^{-1}$ ammonium nitrate treatment, of cumulative N_2O emissions over 50 days in Signor et al. (2013) treatments—as estimated using the nearest weather station (A) and interpolated (B) climate datasets either with (light points) or without (dark points) the use of reported precipitation data—alongside daily measured (red line) versus modeled (blue and green lines) N_2O emissions in the 60 and 80 kg $N ha^{-1}$ ammonium nitrate treatments (C & D, respectively), considering only climate datasets where reported precipitation data were included. Cumulative emissions all showed significant relationships between measured and modeled values, with intercepts that did not differ significantly from 0 (adjusted $r^2=0.62$, $p=0.012$, $RMSE=3295$, intercept = -38 and adjusted $r^2=0.65$, $p=0.0094$, $RMSE= 5200$, intercept=197, original versus with reported climate data, A; adjusted $r^2=0.70$, $p=0.0057$, $RMSE=2200$, intercept = 1394 and adjusted $r^2=0.61$, $p=0.013$, $RMSE= 4000$, intercept=750, B). However, slopes were substantially different, at values of 0.45, 0.05, 0.48 and 0.19, A & B, respectively. DAYCENT successfully simulates the timing of N_2O flux in these treatments (C & D) but increasingly diverges from simulating the magnitude of N_2O flux as N application increases (D).

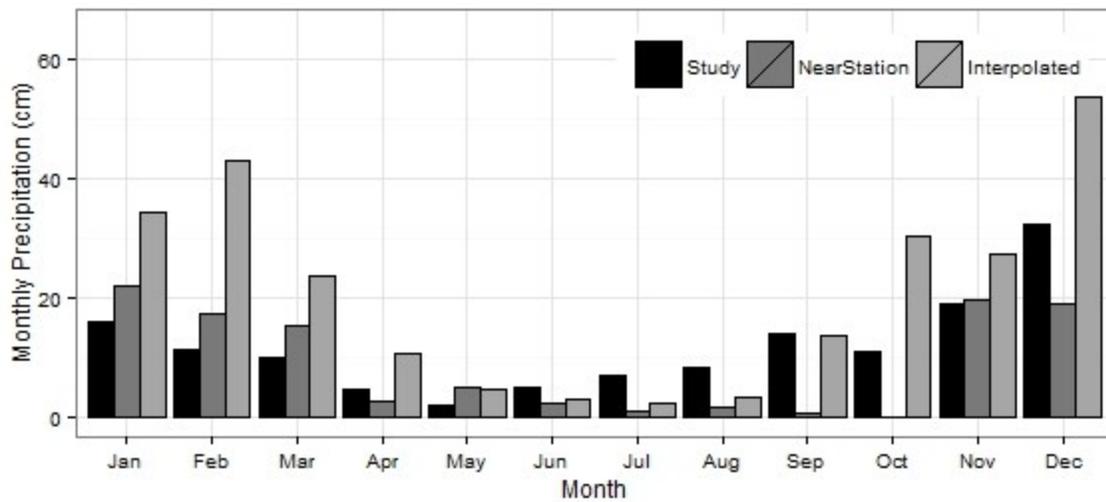


Figure 5-7 Monthly cumulative precipitation for 2009, as reported by Oliveira et al. (2013) (black bars) versus from the nearest weather station and interpolated climate datasets (medium and light bars, respectively). Biases vary by time of year, type of climate data, and climate dataset. Notably, both climate datasets tend to overestimate precipitation in wet months and underestimate precipitation in dry months relative to reported values.

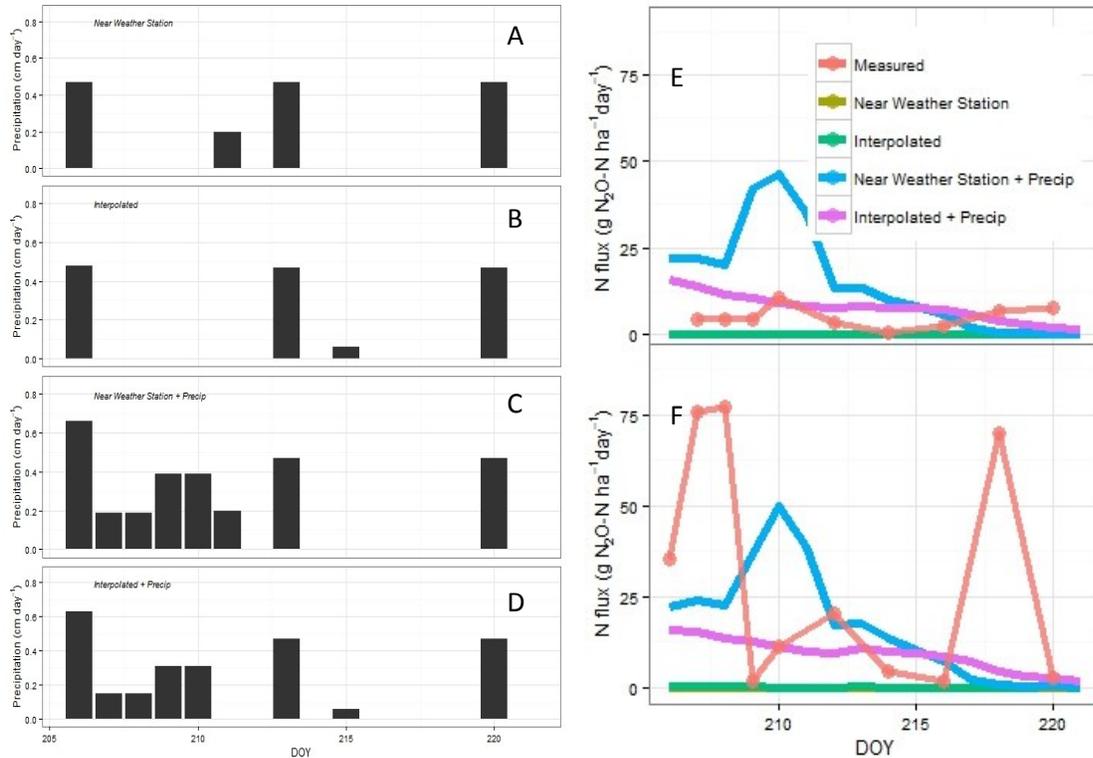


Figure 5-8 Precipitation data used to drive model simulations for the Oliveira et al. (2013) experimental period—as originally reported in the nearest weather station (A) and interpolated (B) climate datasets as well as with the addition of precipitation in the month preceding the experimental period in order to match, by day 210, the reported precipitation for July, 2009 (C & D)—alongside measured versus modeled predictions of daily N₂O emissions from application of water versus vinasse in a burned harvest site (E & F, respectively). Climate drivers both during and preceding the experimental periods can strongly affect DAYCENT simulation of either the magnitude or the timing of high N₂O emissions. Simulated N₂O emissions are more affected by the addition of water than N in these simulations; modeled N₂O emissions are comparable in both treatments in timing and magnitude, while measured values are much lower when only water is applied.

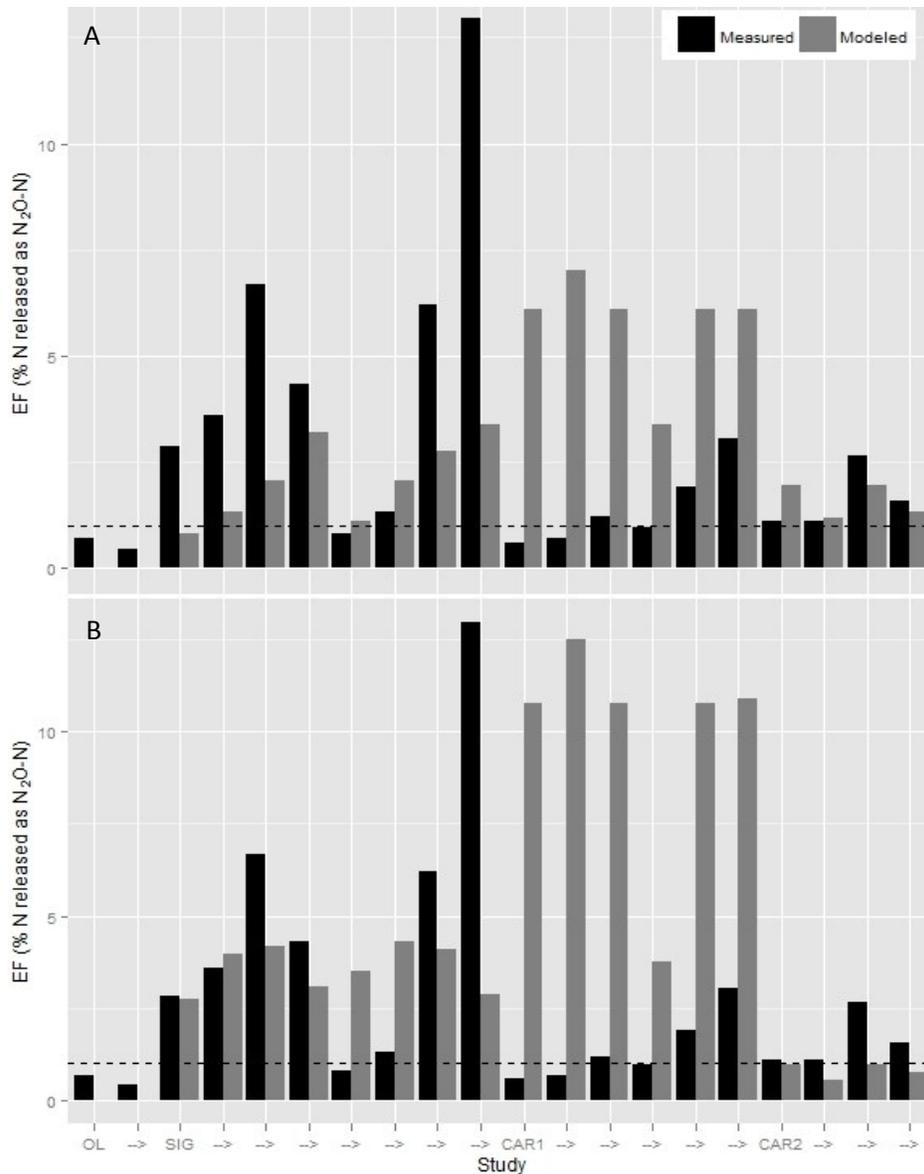


Figure 5-9 Measured versus modeled emission factors (EF) for treatments within each N₂O study, as compared to IPCC emission factor for N addition in agriculture (dotted black line), using nearest weather station climate data (A) versus interpolated climate data (B). On the x-axis, the first treatment in each study is labeled, and all treatments to the right of the label until the subsequent label fall within that study. OL refers to 2 treatments with vinasse additions in Oliveira et al. (2013), SIG to the 8 urea and ammonium nitrate fertilizer addition treatments in Signor et al. (2013), CAR1 to the vinasse + residue return treatments in Piracicaba and CAR2 to the fertilizer treatments in Jaú, respectively, from Carmo et al. (2013). Emission factors are highly variable, with model results under predicting the highest emission factor using both types of climate data. However, interpolated climate data resulted in model predictions that substantially overestimated more treatments (predicting EFs of >5% with 5 treatments (B), versus predicting an EF >5% at only 1 treatment (A)).

6 CONCLUSION

The research presented in this dissertation examines the theory and development of SOM modeling, as well as its application in evaluating crop-based bioenergy production systems when integrated into the DAYCENT ecosystem model. There remains a great deal of uncertainty in how SOM heterogeneity and variability integrates across temporal and spatial scales, e.g. whether mechanisms and empirical relationships known to be of importance at small scales continue to effect cumulative SOM dynamics at larger scales. As a result, SOM modeling structure and approaches must carefully consider the scale at which they are being applied, both in terms of the data used to drive SOM models as well as in terms of model structure and formulation.

The review chapter supported the importance of scale in across advancing areas in SOM modeling development, particularly as SOM models of increasing complexity are integrated into earth system models. Clarification and consistency in the underlying assumptions for either SOM formulation or data used to drive SOM simulations are of high importance for crossing scales from microsite to regional and global levels. Beyond the issue of scale, the review chapter also suggests increasing sophistication in data-model integration in SOM modeling is needed, to capitalize on collaborations across multiple disciplines as well as advances in computational capacity. These efforts can help identify and target SOM measurement and SOM modeling areas where development can maximize advances in the field. The LIDEL analysis provides support for this concept, where the use of a hierarchical Bayesian approach for data-model integration and model parameterization accommodated high variability and uncertainty in measurements as well as in the LIDEL model formulation. The data used for LIDEL model analysis were able to strongly inform three of five unknown parameters, and suggested targeted data evaluating microbial processes during litter decomposition would resolve the high uncertainty for the remaining two parameters. The LIDEL model itself provides an innovative new approach to litter

decomposition simulations that includes both variable microbial CUE and the simulation of microbial products and DOC generation. This is a first step in meeting some of the shortfalls in SOM models discussed in the preceding review chapter.

The final two chapters return to the issue of scale, consistency, and clarity in the application of SOM models to evaluated crop-based bioenergy production systems. In the analysis of corn stover residue removal, DAYCENT model results support the importance of compensating for the removal of biomass with management practices that contribute towards soil C accumulation and storage—e.g. reduced tillage, cover cropping, or additional fertilizer application to increase crop productivity. In the analysis of sugarcane production in Brazil, model results support measured trends in soil C loss with conversion of pasture land into sugarcane production. However, both analyses highlight poor DAYCENT performance simulating N₂O emissions, which are of high concern in estimating the cumulative GHG impact of crop-based bioenergy feedstock production. N₂O emissions are inherently highly temporally and spatially variable. In both analyses DAYCENT model simulations improved at longer temporal scales, although model performance remained poor in treatments where measured N₂O emissions were very high. A comparison of nearest weather station versus interpolated, gridded climate data in the analysis of Brazilian sugarcane highlighted the importance of climate data accuracy in driving DAYCENT model simulations, particularly in the estimation of GHG emissions associated with different management practices.

In summation, this body of work suggests that SOM model theory and development must be carefully connected to their applications in evaluating the GHG impacts of crop-based bioenergy production systems. The application of SOM models in these systems must consider both the scale and assumptions used for SOM model formulation, as well as the scale and assumptions behind data used to drive SOM model simulations. As crop-based biofuels expand globally, this further supports the

importance of collaborative, multi-disciplinary efforts to support SOM model use in these systems, to ensure the strength of their basis on theory for SOM dynamics.

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APPENDIX 1

In this section we detail the hierarchical Bayesian analysis used for the initial conditions of the LIDEL model. We describe the steps of the Monte Carlo Markov chain (MCMC) algorithm used to estimate the posterior distributions of model parameters. We define the notation used to express the process models, data models, and parameter models, and then describe the assumptions for the data and parameter models. We then describe the steps of the MCMC algorithm used in this analysis.

The LIDEL model has 7 pools. The microbial (C_4), microbial products (C_5), and CO_2 (C_7) pools each have an initial value of 0. This analysis estimates the posterior distribution for the latent (“true”) states of the non-lignin structural (C_2) and DOC (C_6) pools, as well as initial litter mass ($L_{iC_M\tau}$) based on parameters for the fraction of initial litter C that is soluble (f_{S_i}), the fraction of soluble material that bypasses all processes reflected in the LIDEL model when exposed to water (f_{DOC}), and the fraction of initial litter C that is lignin (f_{LG_i}). The initial values for the soluble (C_1) and lignin (C_3) LIDEL pools are then calculated by using the posterior distribution of these parameters and the initial litter mass latent state.

A1.1 Definitions

i = litter type (alfalfa, ash, bluestem, oak pine)

k = measurement replicate

L = latent state, or the 'true' underlying condition of the C mass

z = process model state

s = index for pools in the LIDEL model linked to measured data; $s = C_2, C_6$, where C_2 indicates the non-lignin structural (NLS) pool, and C_6 indicates the DOC pool

τ = initial time point, where $day = 0$

f_{DOC} = fraction of DOC, non-microbially released, from plant soluble C

f_{S_i} = fraction of plant soluble carbon (C) by litter type (i)

f_{LIG_i} = fraction of lignin C by litter type (i)

A1.2 Data models

The % C fraction measurements were assumed to have beta distributions, which have shape parameters calculated by moment matching the mean of the f_{S_i} or f_{LIG_i} parameters and the variance of the given measurement type (σ_{HWE}^2 , σ_{DIF}^2 , σ_{LIG}^2).

$y_{HWE_{ik}}$ = extraction measurement of soluble litter C, as % C in hot water extracted material.

These measurements were drawn from Soong et al. (2015) as well as a review of published literature.

$$y_{HWE_{ik}} \sim \text{beta}(g(f_{S_i}, \sigma_{HWE}^2))$$

$y_{DIF_{ik}}$ = mass difference measurement of soluble litter C, as % remaining material after acid detergent fiber digestion. These measurements were drawn from Soong et al. (2015) as well as a review of published literature.

$$y_{DIF_{ik}} = \text{beta}(g(f_{S_i}, \sigma_{DIF}^2))$$

$y_{LIG_{ik}}$ = % acid unhydrolyzable residue C, with acid detergent fiber digestion method. These measurements were drawn from Soong et al. (2015)

$$y_{LIG_{ik}} = \text{beta}(g(f_{LIG_i}, \sigma_{LIG}^2))$$

$y_{iC_M\tau k}$ = mass of C in initial litter, drawn from Soong et al. (2015). This measurement is assumed to be normally distributed, with a mean and a variance determined by the latent state of the litter mass and the measurement error, where:

$$y_{iC_M\tau k} = \text{normal}(L_{iC_M\tau}, \sigma_{y_{C_M i}}^2).$$

$y_{iC_2\tau k}$ = mass of the cellulose and hemicellulose C in initial litter mass, using acid detergent fiber digestion, taken from Soong et al. (2015). In the LIDEL model we chose to define the non-lignin structural (NLS) pool (C_2) as everything remaining when the lignin pool and the soluble pool had been removed. However this pool is predominantly cellulose and hemicellulose. Therefore the direct

measurement of cellulose and hemicellulose was assumed to be a reasonable approximation for the size of the NLS pool. This measurement could not be used for the temporal dynamics analysis because hemicellulose was not measured at subsequent time points. This measurement is assumed to be normally distributed, with a mean and a variance determined by the latent state of the cellulose plus the hemicellulose mass and the measurement error, where;

$$y_{iC_2\tau k} = normal(L_{iC_2\tau}, \sigma_{yC_2i}^2)$$

$$y_{iC_6\tau k} = \text{mass of cumulative DOC as of day 10 of the experiment, taken from Soong et al. (2015).}$$

Conceptually, the initial value of the DOC (C_6) pool in the LIDEL model is representative of soluble litter C that is released immediately with exposure to water, without any exposure to microbial processes. Thus the initial value of this pool indicates the quantity of litter C that bypasses all processes simulated in the LIDEL model. This is an unknown and unmeasured value that conceptually important but extremely difficult to observe directly. However given changes in DOC chemistry observed in Soong et al. (2015) we made the assumption that the DOC released in the first 10 days of the experiment is a reasonable approximation. These data were assumed to be normally distributed, with a mean and variance determined by the latent state of the initial DOC mass and measurement error, where:

$$y_{iC_6\tau k} = normal(L_{iC_6\tau}, \sigma_{yC_6i}^2)$$

A1.3 Process models

Models for the initial state of the non-lignin structural (C_2) and DOC (C_6) LIDEL model pools.

$$z_{iC_2\tau} = L_{iC_M\tau} \left(1 - (f_{s_i} + f_{LIG_i}) \right) + \varepsilon_2, \text{ where } \varepsilon_2 = normal(0, \sigma_{C_2}^2), \text{ and}$$

$$z_{iC_6\tau} = L_{iC_M\tau} * f_{DOC} * f_{s_i} + \varepsilon_6, \text{ where } \varepsilon_6 = normal(0, \sigma_{C_6}^2)$$

A1.4 Parameter models

We assumed the latent states for the non-lignin structural (C_2) and DOC (C_6) pools to be normally distributed, with a mean of the process model prediction and a variance based on model error:

$$L_{iC_2\tau} \sim normal(g(f_{s_i}, f_{LIG_i}, L_{iC_M\tau}), \sigma_{C_2}^2), \text{ and}$$

$$L_{iC_6\tau} \sim \text{normal}(g(f_{DOC}, f_{S_i}, L_{iC_M\tau}), \sigma_{C_6}^2).$$

The % soluble C in the initial litter pool as well as the % lignin C are assumed to have beta distributions, but given uninformative priors due to lack of knowledge. Therefore:

$$f_{S_i} \sim \text{beta}(1,1), \text{ and}$$

$$f_{LIG_i} \sim \text{beta}(1,1).$$

The % soluble C in the initial DOC pool is assumed to have a beta distribution, but is given an uninformative prior due to the lack of knowledge of this parameter. Therefore:

$$f_{DOC} \sim \text{beta}(1,1).$$

For total litter mass, we assume an uninformative uniform prior distribution on the Latent state, in units of g C as;

$$L_{iC_M\tau} \sim \text{uniform}(\min = 1, \max = 1500).$$

Measured and modeled variance terms for all mass values were assumed to have inverse gamma distributions. Measurement variances for $\sigma_{y_{C_Mi}}^2$, $\sigma_{y_{C_2i}}^2$, and $\sigma_{y_{C_6i}}^2$ were given informative priors based on known measurement error in the instruments used to collect observations, at 5-10% of the quantity measured. Informative priors were calculated by determining the two variance terms that placed 95% of the normal distribution within either 5 or 10%, respectively, of the mean of all measurements for each litter type. The shape parameters were then calculated assuming that 95% of the inverse gamma distribution for the variance was within these two variance values. Model variances were given uninformative priors. Therefore;

$$\sigma_{y_{C_2i}}^2 \sim \text{inverse gamma}(\alpha_{2i}, \beta_{2i}) \text{ where;}$$

$$\alpha_2 = (8.5, 8.5, 8.5, 8.5, 8.5) \text{ and } \beta_2 = (337.1, 968.6, 2842.8, 953.1, 1152.6),$$

$$\sigma_{y_{C_6i}}^2 \sim \text{inverse gamma}(\alpha_{6i}, \beta_{6i}) \text{ where;}$$

$$\alpha_6 = (8.5, 8.5, 8.5, 8.5, 8.5) \text{ and } \beta_6 = (116.4, 77.4, 10.5, 17.3, 3.9),$$

$$\sigma_{y_{C_Mi}}^2 \sim \text{inverse gamma}(\alpha_{Mi}, \beta_{Mi}) \text{ where;}$$

$\alpha_M = (8.5, 8.5, 8.5, 8.5, 8.5)$ and $\beta_M = (7684.9, 8550.5, 7670.9, 8912.4, 10815.0)$, and in units of grams carbon as

$$\sigma_C^2 \sim \text{uniform}(\min = 1, \max = 100).$$

The informative prior alpha and beta terms reported above are for the variance of the mass measurements, in units of grams carbon.

The variance terms for all fractional measurements were assumed to have beta distributions, and were given uninformative priors. Therefore:

$$\sigma_{HWE}^2 \sim \text{beta}(1,1),$$

$$\sigma_{DIF}^2 \sim \text{beta}(1,1), \text{ and}$$

$$\sigma_{LIG}^2 \sim \text{beta}(1,1).$$

A1.5 Monte Carlo Markov chain algorithm

The joint posterior distribution for the latent states and parameters described above, given the observations, can be expressed as:

$$\begin{aligned} & [f, \alpha, \beta, L, \sigma_z^2, \sigma_y^2 | y] \propto \\ & \prod_{s=1}^S \prod_{i=1}^I \prod_{k=1}^K [y_{iC_s\tau k} | L_{iC_s\tau}, \sigma_{yC_s i}^2] X [y_{HWE ik} | g(f_{s_i}, \sigma_{HWE}^2)] X [y_{DIF ik} | g(f_{s_i}, \sigma_{DIF}^2)] \\ & X [y_{LIG ik} | g(f_{LIG i}, \sigma_{LIG}^2)] X [L_{iC_2\tau} | g(f_{s_i}, f_{LIG i}, L_{iC_M\tau}), \sigma_{C_2}^2] X [L_{iC_6\tau} | g(f_{DOC}, f_{s_i}, L_{iC_M\tau}), \sigma_{C_6}^2] \\ & X [L_{iC_M\tau} | 1, 1500] X [f_{s_i} | 1, 1] X [f_{LIG i} | 1, 1] X [f_{DOC} | 1, 1] X [\sigma_{yC_2 i}^2 | \alpha_{2i}, \beta_{2i}] \\ & X [\sigma_{yC_6 i}^2 | \alpha_{6i}, \beta_{6i}] X [\sigma_{yC_M i}^2 | \alpha_{Mi}, \beta_{Mi}] X [\sigma_{HWE}^2 | 1, 1] X [\sigma_{DIF}^2 | 1, 1] X [\sigma_{LIG}^2 | 1, 1] X [\sigma_{C_s}^2 | 1, 100] \end{aligned}$$

We approximated the marginal posterior distributions for each latent state and parameter using a random-walk Metropolis Hastings Markov Chain-Monte Carlo (MCMC) algorithm. We present the steps of the MCMC algorithm in the following section.

Step 1. $f, \alpha, \beta, L, \sigma_z^2, \sigma_y^2$ parameters and latent variables are initialized with starting values.

Step 2. The soluble fraction parameter vector (f_{S_i}) is updated in order for each individual litter type, based on the conditional distribution given by

$$[f_{S_i} | \cdot] \propto \prod_{k=1}^K \left[[y_{HWE_{ik}} | g(f_{S_i}, \sigma_{HWE}^2)] [y_{DIF_{ik}} | g(f_{S_i}, \sigma_{DIF}^2)] \right] [L_{iC_2\tau} | g(f_{S_i}, f_{LIG_i}, L_{iC_M\tau}), \sigma_{C_2}^2] \\ [L_{iC_6\tau} | g(f_{DOC}, f_{S_i}, L_{iC_M\tau}), \sigma_{C_6}^2] [f_{S_i} | 1, 1].$$

Step 3. The lignin fraction parameter vector (f_{LIG_i}) is updated in order for each individual litter type, based on the conditional distribution given by

$$[f_{LIG_i} | \cdot] \propto \prod_{k=1}^K [y_{LIG_{ik}} | g(f_{LIG_i}, \sigma_{LIG}^2)] [L_{iC_2\tau} | g(f_{S_i}, f_{LIG_i}, L_{iC_M\tau}), \sigma_{C_2}^2] [f_{LIG_i} | 1, 1].$$

Step 4. Individual litter value for latent variables for $L_{iC_M\tau}$ are updated in succession based on its conditional distribution, given by

$$[L_{iC_M\tau} | \cdot] \propto \prod_{k=1}^K [y_{iC_M\tau k} | L_{iC_M\tau}, \sigma_{yC_Mi}^2] [L_{iC_2\tau} | g(f_{S_i}, f_{LIG_i}, L_{iC_M\tau}), \sigma_{C_2}^2] \\ [L_{iC_6\tau} | g(f_{DOC}, f_{S_i}, L_{iC_M\tau}), \sigma_{C_6}^2] [L_{iC_M\tau} | 1, 1500]$$

Step 5. Measurement and model variance are then updated in succession, given by the conditional distributions

$$[\sigma_{yC_Mi}^2 | \cdot] \propto \prod_{k=1}^K [y_{iC_M\tau k} | L_{iC_M\tau}, \sigma_{yC_Mi}^2] [\sigma_{yC_Mi}^2 | \alpha_{Mi}, \beta_{Mi}], \\ [\sigma_{yC_2i}^2 | \cdot] \propto \prod_{k=1}^K [y_{iC_2\tau k} | L_{iC_2\tau}, \sigma_{yC_2i}^2] [\sigma_{yC_2i}^2 | \alpha_{2i}, \beta_{2i}], \\ [\sigma_{yC_6i}^2 | \cdot] \propto \prod_{k=1}^K [y_{iC_6\tau k} | L_{iC_6\tau}, \sigma_{yC_6i}^2] [\sigma_{yC_6i}^2 | \alpha_{6i}, \beta_{6i}].$$

Step 6. Individual litter value for latent variables for $L_{iC_2\tau}$ are updated in succession based on its conditional distribution, given by

$$[L_{iC_2\tau} | \cdot] \propto \prod_{k=1}^K [y_{iC_2\tau k} | L_{iC_2\tau}, \sigma_{yC_2i}^2] [L_{iC_2\tau} | g(f_{s_i}, f_{LIG_i}, L_{iC_M\tau}), \sigma_{C_2}^2],$$

followed by litter values in succession for $L_{iC_6\tau}$ given by

$$[L_{iC_6\tau} | \cdot] \propto \prod_{k=1}^K [y_{iC_6\tau k} | L_{iC_6\tau}, \sigma_{yC_6i}^2] [L_{iC_6\tau} | g(f_{DOC}, f_{s_i}, L_{iC_M\tau}), \sigma_{C_6}^2].$$

Step 7. After step 6, parameters not individual to litter type (scalars) are then updated. This first includes the scalar for f_{DOC} , given by the conditional distribution as

$$[f_{DOC} | \cdot] \propto [L_{iC_6\tau} | g(f_{DOC}, f_{s_i}, L_{iC_M\tau}), \sigma_{C_6}^2] [f_{DOC} | 1, 1].$$

Step 8. Measurement and model variance are then updated in succession, given by the conditional distributions

$$[\sigma_{C_6}^2 | \cdot] \propto \prod_{i=1}^I [L_{iC_6\tau} | g(f_{DOC}, f_{s_i}, L_{iC_M\tau}), \sigma_{C_6}^2] [\sigma_{C_6}^2 | 1, 100],$$

$$[\sigma_{C_2}^2 | \cdot] \propto \prod_{i=1}^I [L_{iC_2\tau} | g(f_{s_i}, f_{LIG_i}, L_{iC_M\tau}), \sigma_{C_2}^2] [\sigma_{C_2}^2 | 1, 100],$$

$$[\sigma_{HWE}^2 | \cdot] \propto \prod_{k=1}^K [y_{HWE_{ik}} | g(f_{s_i}, \sigma_{HWE}^2)] [\sigma_{HWE}^2 | 1, 1],$$

$$[\sigma_{DIF}^2 | \cdot] \propto \prod_{k=1}^K [y_{DIF_{ik}} | g(f_{s_i}, \sigma_{DIF}^2)] [\sigma_{DIF}^2 | 1, 1],$$

$$[\sigma_{LIG}^2 | \cdot] \propto \prod_{k=1}^K [y_{LIG_{ik}} | g(f_{LIG_i}, \sigma_{LIG}^2)] [\sigma_{LIG}^2 | 1, 1].$$

Step 9. Repeat steps 1-8 many times.

To simplify the number of parameters being estimated in this analysis, the initial values for the soluble (C_1) and lignin (C_3) LIDEL model pools were then calculated based on posterior distributions for $L_{iC_M\tau}$, f_{s_i} , f_{DOC} , and f_{LIG_i} , since these pools did not have additional data to estimate the underlying latent states.

$$z_{iC_1\tau} = (L_{iC_M\tau} * f_{S_i}) - (L_{iC_M\tau} * f_{S_i} * f_{DOC})$$

$$z_{iC_3\tau} = L_{iC_M\tau} * f_{LIG_i}$$

APPENDIX 2

In this section we describe a hierarchical Bayesian analysis to estimate posterior distributions of parameters in the LIDEL model, as well as the posterior distribution of latent variables and variance components of time series measurement data from Soong et al. (2015). The posterior distributions and analyses are based on initial conditions analysis (Appendix 1) priors to initialize model pools when the LIDEL model is run in the analysis described here. The LIDEL model is presented in the main text and will not be repeated here. We define notation used to express the data and parameter models, and then present the assumptions used to specify the data and parameter models. We then describe the steps of the MCMC algorithm used in this analysis.

A2.1 Definitions

i = litter types (alfalfa, ash, bluestem, oak pine)

k = measurement replicate

L = latent state, or the 'true' underlying condition of the variable

s = index for states in the LIDEL model linked to measured data; $s = C_M, C_6, C_7$, where C_M indicates the total mass of the 3 litter pools plus the microbes and microbial products pools, C_6 indicates the DOC pool, and C_7 indicates the CO_2 pool

τ = initial time point, where $day = 0$

l = *index* measures of a given s , from 1-n measurements in increments of 1

d_l = *day* at which l - indexed measurement is taken. The time interval between measurements can therefore be calculated using the notation $d_l - \Delta d_{l-1}$.

θ = vector of the 5 parameters of interest in this analysis: the decay of the soluble (k_1), non-soluble structural (k_2), and microbial biomass pools (k_4), the generation of microbial products from microbe biomass (β_3), and the generation of DOC from the decay of microbe biomass (λ_2).

A2.2 Data models

All measures of litter C mass were assumed to be normally distributed, with a mean of the latent variable corresponding to the 'true' state of that measurement and variance based on the measurement error associated with the instrument used to take the observation. Therefore:

$$y_{iC_M d_l k} \sim \text{normal}(L_{iC_M d_l}, \sigma_{y_{iC_M d_l}}^2),$$

$$y_{iC_6 d_l k} \sim \text{normal}(L_{iC_6 d_l}, \sigma_{y_{iC_6 d_l}}^2), \text{ and}$$

$$y_{iC_7 d_l k} \sim \text{normal}(L_{iC_7 d_l}, \sigma_{y_{iC_7 d_l}}^2).$$

A2.3 Parameter models

We assume a normal distribution for all latent variables, with a mean of the LIDEL model prediction at a given measurement time point and variance based on model error for that time point and model state. Therefore:

$$L_{iC_M d_l} \sim \text{normal}(g(\boldsymbol{\theta}, L_{iC_M d_l - \Delta d_{l-1}}), \sigma_{C_M d_l}^2),$$

$$L_{iC_6 d_l} \sim \text{normal}(g(\boldsymbol{\theta}, L_{iC_6 d_l - \Delta d_{l-1}}), \sigma_{C_6 d_l}^2), \text{ and}$$

$$L_{iC_7 d_l} \sim \text{normal}(g(\boldsymbol{\theta}, L_{iC_7 d_l - \Delta d_{l-1}}), \sigma_{C_7 d_l}^2).$$

All five parameters of interest in this analysis are rates (expressed as a fraction day⁻¹). Therefore all five parameters were assumed to have beta distributions and were given uninformative priors, where:

$$\theta_i \sim \text{beta}(1,1).$$

Measured and modeled variance terms were assumed to have inverse gamma distributions. Measurement variances were given informative priors based on known measurement error in the instruments used to collect observations. Model variances were given uninformative priors. Therefore;

$$\sigma_{C_s d_l}^2 \sim \text{inverse gamma}(0.001, 0.001), \text{ and}$$

$$\sigma_{y_{iC_s d_l}}^2 \sim \text{inverse gamma}(\alpha_{iC_s d_l}, \beta_{iC_s d_l}).$$

A2.4 Monte Carlo Markov chain algorithm

The joint posterior distribution for the latent states and parameters described above, given the observations, can be expressed as:

$$\begin{aligned}
 & [\boldsymbol{\theta}, \mathbf{L}, \boldsymbol{\sigma}_C^2, \boldsymbol{\sigma}_y^2 | \mathbf{y}] \propto \\
 & \prod_{i=1}^I \prod_{s=1}^S \prod_{l=2}^L \prod_{k=1}^K [y_{isd_ik} | L_{isd_l}, \sigma_{y_{isd_l}}^2] X [L_{isd_l} | g(\boldsymbol{\theta}, L_{isd_l - \Delta d_{l-1}}), \sigma_{C_s d_l}^2] X [L_{isd_1} | g(\boldsymbol{\theta}, L_{is\tau}), \sigma_{C_s d_l}^2] \\
 & X [\sigma_{C_s d_l}^2 | 0.001, 0.001] X [\sigma_{y_{ic_s d_l}}^2 | \alpha_{ic_s d_l}, \beta_{ic_s d_l}] X [\theta_i | 1, 1]
 \end{aligned}$$

We estimated posterior distributions for each latent state and parameter using a random-walk Metropolis Hastings within a Markov Chain-Monte Carlo (MCMC) algorithm. We present the steps of the MCMC algorithm in the following section.

Step 1. $\boldsymbol{\theta}, \mathbf{L}, \boldsymbol{\sigma}_C^2, \boldsymbol{\sigma}_y^2$ parameters and latent variables are each initialized with an estimated starting value.

Step 2. The latent variables for C_M, C_6 and C_7 are updated for all measurement time points and model pools across litter types by iterating across the l indices. For C_M , the two measured time points (day 95 and day 365) of mass remaining in the incubation experiment correspond to the sum of five LIDEL model pools (C_1 - C_5). However the litter mass (C_M) measurements at these time points are not paired with sufficient data to inform how measures of litter mass are fractionated across these five LIDEL model pools. Therefore the day 95 and day 365 C_M measurements can only be informed by the initial model values, where sufficient fractionation data allowed for the posterior distribution of each individual LIDEL model pool to be estimated. The conditional distribution for the C_M latent variables are therefore given by

$$[L_{iC_M d_l} | \cdot] \propto [L_{iC_M d_l} | g(\boldsymbol{\theta}, L_{is\tau}), \sigma_{C_M d_l}^2] \prod_{k=1}^K [y_{iC_M d_l k} | L_{iC_M d_l}, \sigma_{y_{iC_M d_l}}^2].$$

The latent variables for C_6 and C_7 , however, are informed by measurements that correspond to these individual pools through time. Therefore, except for the initial and final time measurements, the conditional distribution of a given latent variable at a given point in time must consider both the previous and the subsequent time point.

At $l = 1$, the conditional distribution is given by

$$[L_{isd_1} | \cdot] \propto [L_{isd_{l+\Delta d_{l+1}}} | g(\boldsymbol{\theta}, L_{isd_1}), \sigma_{C_s d_{l+1}}^2] [L_{isd_1} | g(\boldsymbol{\theta}, L_{is\tau}), \sigma_{C_s d_1}^2] \prod_{k=1}^K [y_{isd_{1k}} | L_{isd_1}, \sigma_{y_{ic_s d_1}}^2].$$

When $l = 1$ is between 2 and L , the conditional distribution is given by

$$[L_{isd_l} | \cdot] \propto [L_{isd_l} | g(\boldsymbol{\theta}, L_{isd_{l-\Delta d_{l-1}}}), \sigma_{C_s d_l}^2] [L_{isd_{l+\Delta d_{l+1}}} | g(\boldsymbol{\theta}, L_{isd_l}), \sigma_{C_s d_{l+1}}^2] \prod_{k=1}^K [y_{isd_{lk}} | L_{isd_l}, \sigma_{y_{ic_s d_l}}^2]$$

When $l = L$ the conditional distribution is given by

$$[L_{isd_L} | \cdot] \propto [L_{isd_L} | g(\boldsymbol{\theta}, L_{isd_{l-\Delta d_{l-1}}}), \sigma_{C_s d_L}^2] \prod_{k=1}^K [y_{isd_{Lk}} | L_{isd_L}, \sigma_{y_{ic_s d_L}}^2].$$

Step 3. The each of the five LIDEL parameters is then updated sequentially, each based on the conditional distribution given by

$$[\theta_i | \cdot] \propto [L_{isd_L} | g(\boldsymbol{\theta}, L_{isd_{l-\Delta d_{l-1}}}), \sigma_{C_s d_L}^2] \prod_{i=1}^I \prod_{s=1}^S \prod_{l=2}^L [L_{isd_l} | g(\boldsymbol{\theta}, L_{isd_{l-\Delta d_{l-1}}}), \sigma_{C_s d_l}^2] \prod_{i=1}^I \prod_{s=1}^S [L_{isd_1} | g(\boldsymbol{\theta}, L_{is\tau}), \sigma_{C_s d_1}^2] [\theta_i | 1, 1].$$

Step 4. Measurement and model variance are then updated in succession, given by the conditional distributions

$$[\sigma_{y_{ic_s d_l}}^2 | \cdot] \propto \prod_{k=1}^K [y_{isd_{lk}} | L_{isd_l}, \sigma_{y_{ic_s d_l}}^2] [\sigma_{y_{ic_s d_l}}^2 | \alpha_{ic_s d_l}, \beta_{ic_s d_l}]$$

$$[\sigma_{C_s d_l}^2 | \cdot] \propto \prod_{i=1}^l [L_{isd_l} | g(\boldsymbol{\theta}, L_{isd_l} - \Delta d_{l-1}), \sigma_{C_s d_l}^2] [\sigma_{C_s d_l}^2 | 0.001, 0.001].$$

Step 5. Repeat steps 1-4 many times.