OPINION

A big-microsite framework for soil carbon modeling

ERIC A. DAVIDSON[1], KATHLEEN E. SAVAGE[1] and ADRIEN C. FINZI[2]

[1]*Woods Hole Research Center, 149 Woods Hole Road, Falmouth, MA 02540-1644, USA,* [2]*Department of Biology, Boston University, Boston, MA 02215, USA*

Abstract

Soil carbon cycling processes potentially play a large role in biotic feedbacks to climate change, but little agreement exists at present on what the core of numerical soil C cycling models should look like. In contrast, most canopy models of photosynthesis and leaf gas exchange share a common 'Farquhaur-model' core structure. Here, we explore why a similar core model structure for heterotrophic soil respiration remains elusive and how a pathway to that goal might be envisioned. The spatial and temporal variation in soil microsite conditions greatly complicates modeling efforts, but we believe it is possible to develop a tractable number of parameterizable equations that are organized into a coherent, modular, numerical model structure. First, we show parallels in insights gleaned from linking Arrhenius and Michaelis–Menten kinetics for both photosynthesis and soil respiration. Additional equations and layers of complexity are then added to simulate substrate supply. For soils, model modules that simulate carbon stabilization processes will be key to estimating the fraction of soil C that is accessible to enzymes. Potential modules for dynamic photosynthate input, wetting-event inputs, freeze–thaw impacts on substrate diffusion, aggregate turnover, soluble-C sorption, gas transport, methane respiration, and microbial dynamics are described for conceptually and numerically linking our understanding of fast-response processes of soil gas exchange with longer-term dynamics of soil carbon and nitrogen stocks.

Keywords: carbon cycle, CH_4, CO_2, DAMM model, methane oxidation, soil enzymes, soil organic matter, soil respiration

Received 23 April 2014 and accepted 17 June 2014

Introduction

Heterotrophic respiration in terrestrial ecosystems, which mostly occurs within the soil, has long been recognized as a potential positive feedback to climate change (Schlesinger, 1977; Woodwell, 1983; Jenkinson *et al.*, 1991; Raich & Schlesinger, 1992). These papers and many published since then include conceptual and numerical models of soil organic matter (SOM) decomposition and CO_2 efflux that range in complexity, including simple Q_{10} functions, statistical relationships based on global analyses of temperature, precipitation, and net primary productivity, and relatively complex soil biogeochemistry models of multiple soil C pools decaying according to numerical functions.

In this same era of 1970s–1980s C-cycle research, a seminal paper was published that described photosynthesis using a series of relatively few equations (Farquhar *et al.*, 1980). The 'Farquhar model' has since become a widely used core structure of numerical models of varying complexity that simulate canopy processes at a variety of scales, from chloroplasts to the globe. In

Correspondence: Eric A. Davidson, tel. + 1/508 444 1532, fax + 1/508 444 1832, e-mail: edavidson@whrc.org

contrast, the few soil biogeochemistry models whose basic model structure have been widely employed by other models (e.g., the CENTURY model structure of soil C pools of differing mean residence times according to first order decay constants, Parton *et al.*, 1987), have been criticized as inadequate for explaining the mechanisms of stabilization of soil C and how C dynamics may change with further global change and at large scales (Schmidt *et al.*, 2011). In any case, little agreement exists on what the core of a numerical soil C cycling model should look like. Furthermore, the wide disparity of soil C simulations and their importance in biotic feedbacks to climate change in current Earth System Models (ESMs) demonstrates the need to improve soil model development (Todd-Brown *et al.*, 2013).

Numerical models express conceptual understanding of ecosystem processes in linked mathematical equations. They enable testing of how well this understanding translates into simulations of current patterns and trends, predictions of responses to perturbations, and identification of knowledge gaps. Practical concerns of finding pertinent data to estimate parameters must be kept in mind when selecting equations. Some equations are derived from statistical fits of observational data; others are first derived from a theoretical basis and

then compared to observational data; and many result from iterations of observation and theoretical interpretation. In this paper, we explore why a 'Farquhaur-model-equivalent' for heterotrophic soil respiration remains elusive and how a pathway to that goal might be envisioned.

The Gemish effect

The most convenient excuse for not being able to simulate soil C dynamics in a parsimonious model is that soils are such a gemish of varying types of organic compounds, minerals, and organisms (one could find a definition of 'gemish' in the Yiddish Journal of Soil Science Glossary, if only there were one, so we leave the reader to find one of the widely available and delightful online or in-person translators). In addition to the huge and largely unknown variation in microbial diversity within the soil, the physical and chemical diversity of microsites, including pH, Eh, O_2, dissolved organic carbon and nitrogen (DOC, DON) – just to name a few – are legend. To 'model decay rate as function of substrate properties and positions in microenvironment, microbial activity, and soil conditions including pH, temperature and moisture' (Schmidt et al., 2011), these processes must be represented in a tractable number of parameterizable equations that are organized into a coherent numerical model structure.

Unlike the soil gemish, plant physiologists can usually study a whole organism or intact organ of an organism, such as a leaf, stem, or root, and carefully control its environment while studying it. Furthermore, CO_2 and H_2O are the only substrates, although intermediate substrates are produced and consumed and other nutrients are needed for enzymatic capacity. Leaf exchange of gases can be measured under controlled temperature, humidity, CO_2, and light within a cuvette while the leaf is still attached to the plant *in situ*! In contrast, while some soil microorganisms can be isolated, most have probably not been successfully cultured, and taking them out of their native gemish may change their physiology. Laboratory estimates of kinetic parameters of enzymes purified from soil samples tend to differ from those utilized in decomposition models calibrated with field data (Wang et al., 2013).

Variation among soil microsite conditions is often invoked when explaining unexpected observations, such as CH_4 production in a well-aerated soil or autotrophic nitrification in a very acidic soil. Attribution of unexpected patterns of soil processes to the presence of highly variable soil microsites may be correct, but can these microsite processes be scaled effectively for use in numerical soil C models and ESMs?

The kinetics we know

The microsite of an enzymatic reaction is a place where substrate [S] meets enzyme [E]; they form a reversible complex [E−S]; and then an irreversible reaction may occur that forms one or more products and liberates the enzyme [E + P]. Examples include the depolymerization of an organic molecule in the soil or the carboxylation of a molecule within a chloroplast. This theory of enzymatic reaction led Leonor Michaelis and Maud Menten to develop an equation (Michaelis & Menten, 1913) that describes how the velocity (V) of an enzymatic reaction depends on the maximum velocity of the reaction (V_{max}), the substrate concentrations [S], and first and second order rate constants for the breakdown and formation of the enzyme–substrate complex. The rate constants mathematically collapse into what has become known as the half-saturation constant or the Michaelis–Menten constant, K_m:

$$V = V_{max} \times \frac{[S]}{K_m + [S]} \qquad (1)$$

An emergent property of the K_m is that it provides an index for the affinity of the enzyme for the substrate. Although this equation is based on theory, the parameters V_{max} and K_m, must be fitted empirically.

The M–M equation has been applied empirically to many other processes, such as growth of microbial populations (Monod, 1949), Langmuir sorption equation (Mayes et al., 2012), and physiology of muscle contraction (Sorensen & Novak, 1996). In the latter example, muscle is the enzyme-equivalent and electrical stimulation is the substrate-equivalent. Experimental results follow M–M kinetics remarkably well because the muscle can become saturated by abundant electrical simulation, just as an enzyme becomes saturated with substrate. In this example, an empirical relationship that shares a form derived from a theory in one field may provide insight for refining theory in another field.

While M–M kinetics describes substrate–enzyme reactions well, temperature is also important, because each of the following may be temperature-dependent: (1) the diffusion of substrate to the enzyme (or vice versa) in water films or in air spaces; (2) the availability of substrate (e.g., thawing of permafrost; drying of wetlands; formation and breakdown of aggregates); (3) the production of carbon substrates by autotrophs (note that 'temperature-dependent' could be substituted by 'climate-dependent' in items 1–3, because soil water content also affects these substrate supply processes; Davidson et al., 1998, 2006); (4) the conformation of the enzyme, and hence its affinity for the substrate; and (5)

the velocity of the reaction [$E-S \rightarrow E + P$], which follows Arrhenius kinetics (Arrhenius, 1889):

$$V = \alpha \times e^{-E_a/RT} \qquad (2)$$

where E_a is the activation energy (see below), R is the universal gas constant and T is the temperature in Kelvin (note that R is commonly used for enzymatic reactions, where the activation energy is given in units of joules per mole, but the Boltzmann constant is used for reactions where units of joules per molecule are used).

Svante Arrhenius's equation is a hybrid between empirical and theory-based. Having studied with van't Hoff, he was aware that reaction rates often roughly double or triple for every 10 °C rise in temperature (i.e., Q_{10} values of about 2–3). However, it is difficult to reconcile this doubling or tripling of reaction rate with the fact that a 10 °C (10 K) change in temperature corresponds to only about a 3% change in kinetic energy of the molecules, which is calculated on the absolute temperature scale (e.g., at 25 °C and 298 K, a change of 10 K is only $10/298 = 3\%$). Arrhenius showed that the important point is not the *average* kinetic energy, but rather the *distribution* of energies of the population of molecules, which follows a Maxwell–Boltzmann function (Hochachka & Somero, 2002). As the whole distribution shifts upwards with an increase in temperature, the subset of molecules with energies large enough for the reaction to occur – defined as those above the E_a – increases disproportionately compared to the average energy. Hence, Q_{10}s of 2 or 3 can be explained mathematically by this function. Moreover, enzymes and other catalysts have the effect of lowering the energy needed for the reaction (*i.e.*, lowering E_a). The exponential term in the Arrhenius equation ($e^{-E_a/RT}$) determines for any given temperature the fraction of the molecules present with energies equal to or in excess of the required activation energy.

The Arrhenius function has enjoyed widespread success for predicting the temperature sensitivity of many kinds of reactions. It has since been mostly reconciled with the fields of collision theory and transition state theory of reactions (Laidler & King, 1983). Nevertheless, experts in many fields still consider that the Arrhenius equation is mostly empirical because of the absence of a strong and thorough theoretical basis, although they admire how useful it has been (Galwey & Brown, 1995). For our purposes regarding heterotrophic soil CO_2 production, the Arrhenius function works well as long as substrate supply is not limiting (Davidson & Janssens, 2006). Unfortunately, the five temperature/climate-dependent effects listed above are often confounded, and these effects are often included, intentionally or unintentionally, in applications of the Arrhenius function to a wide range of observations, even though the equation was meant to apply only to item #5 on the list, the velocity of the enzymatic process itself. As is the case for parameterization of the M–M equation, the pre-exponential (α) and E_a Arrhenius parameters must be fitted empirically.

The parsimonious Farquhar model of photosynthesis employs M–M functions to simulate reactions rates of carboxylase and oxidase, modified by the temperature dependencies of the kinetic properties of these enzymatic as determined by Arrhenius functions. Of course, several additional equations are needed to simulate the availability of substrates at the enzymatic reaction site, especially related to stomatal conductance (Baldocchi & Meyers, 1998). Similarly, beyond a single chloroplast, more model complexity has been added to simulate the number of chloroplasts and their enzymatic capacity in a leaf or in a cropland or forest.

If this combination of Arrhenius and M–M kinetics works well as the starting point for modeling photosynthesis, from the reaction microsites within a chloroplast to the entire forest, why would these well-known kinetic equations not apply similarly to a core understanding of enzymatic activity from soil microsites to soil pedons and larger scales? As is the case for photosynthesis, the dynamics of the various substrates, including their transport to the reaction microsites, presents another component of the modeling challenge. However, we suggest that a good place to start is what is known about the reactions of interest and then consider what regulates the abundance of the substrates and how they get to the reaction sites – or not. If substrates do not come into contact with enzymes, it is likely due to soil C stabilization processes, which therefore should also be incorporated into model structure.

The Dual Arrhenius Michaelis–Menten big microsite

The Dual Arrhenius Michaelis–Menten (DAMM) model for soil respiration (Davidson *et al.*, 2012) is intended to be for gas exchange across soil microsites what an early 'big leaf' model was for gas exchange of a forest, grassland, or cropland canopy (Sellers *et al.*, 1997). Although the term is a bit of an oxymoron, it might be called a 'big microsite' model. At the core of the model is a M–M equation with two substrates for aerobic respiration: a C substrate accessible to an enzyme [S_x] and oxygen [O_2] (Fig. 1). In this early version, all C substrates are considered equally, but one could specify microsites for as many different C substrates [S_1, S_2, S_3 ...] or families of trait-based substrate–enzyme groups (Allison, 2012; Wieder *et al.*, 2014) as data and computational power permit.
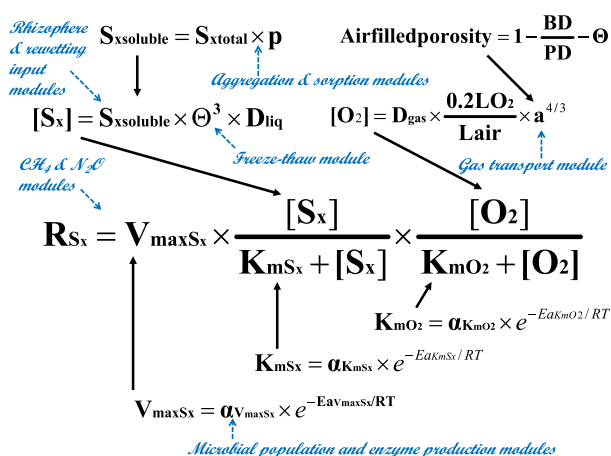
$$S_{xsoluble} = S_{xtotal} \times p$$

Rhizosphere & rewetting input modules

$$Airfilledporosity = 1 - \frac{BD}{PD} - \Theta$$

$$[S_x] = S_{xsoluble} \times \Theta^3 \times D_{liq}$$

Aggregation & sorption modules

$$[O_2] = D_{gas} \times \frac{0.2 LO_2}{L_{air}} \times a^{4/3}$$

CH₄ & N₂O modules

Freeze-thaw module

Gas transport module

$$R_{Sx} = V_{maxSx} \times \frac{[S_x]}{K_{mSx} + [S_x]} \times \frac{[O_2]}{K_{mO2} + [O_2]}$$

$$K_{mO2} = \alpha_{KmO2} \times e^{-EaKmO2/RT}$$

$$K_{mSx} = \alpha_{KmSx} \times e^{-EaKmSx/RT}$$

$$V_{maxSx} = \alpha_{VmaxSx} \times e^{-EavmaxSx/RT}$$

Microbial population and enzyme production modules

Fig. 1 Schematic diagram of the Dual Arrhenius Michaelis–Menten (DAMM) model, redrawn from Davidson *et al.* (2012). Opportunities described in this manuscript for adding modules are shown in blue italicized font.

Canopy models have become more complex since the first big leaf models simulated an entire forest as a single stomate and chloroplast; they now have multiple layers, such as sun and shade leaves, and differentiate among plant functional groups (Baldocchi & Meyers, 1998). Hence, not only does variation in temperature, humidity, and CO_2 concentration affect simulated photosynthesis in modern canopy models, but plant functional traits are also important and variable. Soil carbon models need a similar basis in enzyme kinetics, modified by variation in the traits of the decomposer community. The current generation of decomposition models that depend upon first order decay constants of prescribed soil pools are not well designed to represent both reaction kinetics and changes in reaction agents (Todd-Brown *et al.*, 2012), both of which are likely to

change under most scenarios of global change. In contrast, the DAMM model is designed to enable layers of complexity to be added concerning substrate supply and decomposer communities, including temporal and spatial variation in enzymatic capacity and substrate affinity, as we will show in a section below on a microbial population and enzyme production module.

The V_{max} and K_m parameters of the M–M function in DAMM are functions of temperature, as prescribed by three Arrhenius equations (Fig. 1). The temperature sensitivity of K_m and the appropriate mechanistic or statistical model for it are not clear, but there is empirical and theoretical evidence for a positive relationship (Hochachka & Somero, 2002; German *et al.*, 2012; Stone *et al.*, 2012). Finally, four more equations provide a parsimonious simulation of the diffusivity of soluble-C substrates to the enzyme through soil water films (D_{liq}) (or, conversely, the diffusion of soluble enzymes to insoluble-C substrates) and the diffusivity of O_2 through air-filled pore spaces (D_{gas}; Fig. 1). Air-filled porosity is calculated from bulk density (BD), particle density (PD), and volumetric water content (θ). Note that θ strongly influences the diffusion of substrates, and hence the concentrations of $[S_x]$ and $[O_2]$ used in the M–M equation, whereas temperature affects the Arrhenius functions that determine the values of V_{max} and the K_m's. The resulting temperature–moisture response surface for aerobic respiration, showing the greatest temperature sensitivity expressed at intermediate soil water contents and much lower apparent temperature sensitivity at extreme low and high water contents (Fig. 2a), is an emergent property of linking M–M and Arrhenius equations and these diffusion equations. Similar temperature–moisture response surfaces have been derived in numerous empirical studies using linear and nonlinear statistical curve fitting (Linn
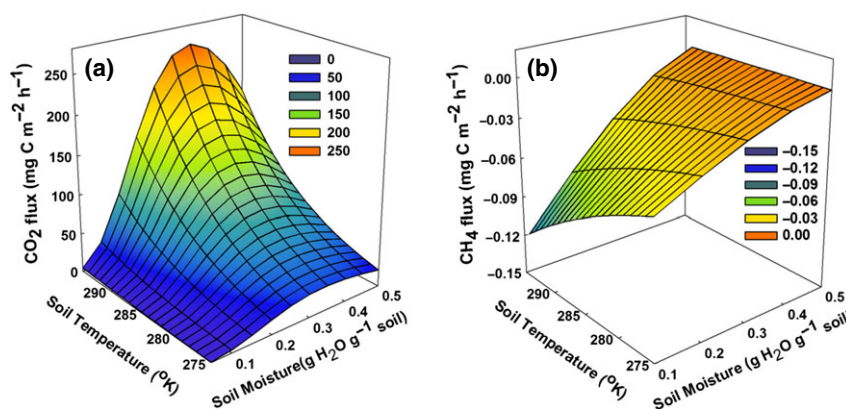

Fig. 2 Temperature and soil moisture response surfaces of the DAMM model for (a) aerobic soil respiration (redrawn from Davidson *et al.*, 2012) and (b) methane oxidation (unpublished simulation by Davidson and Savage). Methane consumption by soil is shown as negative flux values.

& Doran, 1984; Davidson *et al.*, 1998, 2000, 2006; Savage *et al.*, 2009; Moyano *et al.*, 2013), but such empirical fits are seldom applicable beyond the specific study site for which they were derived.

The DAMM model incorporates controls of temperature, soil water content, and substrate supply, which correspond, respectively, to the temperature, precipitation, and net primary production driving variables of soil respiration identified by Raich & Schlesinger (1992) through their statistical analyses of global databases. However, these functions are now in a mathematical form suitable for a 'big microsite' model framework that links M–M and Arrhenius kinetics.

Improving structure and adding layers of complexity

The current model structure and its seven equations shown in Fig. 1 are simplistic and await improvement. While this version of DAMM worked as well or better than any statistical model that we have derived for our field studies of seasonal variation at the Harvard Forest (Davidson *et al.*, 2012), it did not simulate wet-up events well. In its current form, it would not be suitable for several potentially important applications, such as permafrost thaw or methane fluxes. Most importantly, it only addresses fast-response soil heterotrophic respiration processes and is not yet connected to processes related to C inputs or to C stabilization.

Shown in blue italic font in Fig. 1 are six modules that could be added to make the model more robust. Other innovations will hopefully emerge from the scientific community. Adding complexity modularly follows a guiding philosophy of starting with a parsimonious core model structure based as closely as possible on first principles, and adding improvements and layers of complexity as the questions, data, computing power, and understanding warrant (Keenan *et al.*, 2013). Most of the proposed modules deal with substrate input and transport, but some deal with enzyme production, as described in the following - sections.

Rhizosphere inputs and wet-up events

At present, concentrations of substrate-C accessible to enzymes $[S_x]$ are simulated simply as a constant proportion (p) of total soil C (Fig. 1), which we know is not true. A relatively simple modification of the DAMM model has already demonstrated that making $[S_x]$ dynamic improves model performance. Oikawa *et al.* (2014) modified the central M–M equation of DAMM to include three substrates: (1) a fast-response labile-C pool such as recent photosynthate or soil C released following wetting of dry soil; (2) a slow-response SOM pool; and (3) O_2. In a heterotrophic-only version of the revised model, the simulated labile-C pool accumulated during dry periods and then diffused rapidly to reaction microsites upon wetting. The first simulated wetting event after a long dry period produced a large CO_2 pulse, whereas the pulse following a second wetting event a few days later was smaller due to less accumulated labile-C, which was in good agreement with flux measurements. In a mixed hetero-autotrophic model, the authors augmented the soil labile-C pool with simulated photosynthetic inputs from planted sorghum, which were calculated as a function of leaf area index and photosynthetically active radiation. The model was able to simulate measured daily hysteresis in temperature–flux relationships due to lags in plant inputs to the rhizosphere. We are working on a similar approach to link DAMM with photosynthetic inputs from the Forest Biomass, Assimilation, Allocation and Respiration model (FöBAAR; Keenan *et al.*, 2012), which employs a parsimonious canopy and soil model structure. For simulations at larger scales, depth-resolved databases of root biomass and turnover (Schenk & Jackson, 2002, 2003; Gill & Jackson, 2003; Jackson *et al.*, 2003) and root exudation (AC Finzi, RZ Abramoff, KS Spiller, ER Brzostek and RP Phillips, unpublished data) could improve representation of these inputs for soil carbon substrate availability.

Aggregation and sorption

The fraction of total soil C that is exposed to enzymes is influenced strongly by the amount of C that is physically and chemically protected (Oades, 1988; Sollins *et al.*, 1996; Hedges *et al.*, 2000). Although recognized for a long time, stabilization mechanisms are still the subject of much research (Kleber *et al.*, 2007; Sollins *et al.*, 2007; Schmidt *et al.*, 2011). This incomplete understanding impedes the expression of emerging conceptual models in mathematical form for use in numerical models. However, this is precisely what is needed if fast-response C-cycle models based on fundamental kinetics are to be linked to longer-term processes of soil C stabilization and de-stabilization. Because the DAMM model specifically simulates the coupling of substrate and enzyme, there is also an opportunity to simulate the flip side – i.e., the physical disconnect between decomposers and organic matter.

Conceptual models have been developed (Six & Paustian, 2014) and partially implemented in a numerical model (Segoli *et al.*, 2013), indicating that the fraction of microaggregates within macroaggregates could be used as a measurable parameter related to C protected within aggregates. A model module of aggregate formation and breakdown could generate

estimates of the fraction of C inputs not protected by aggregates and the rate of C exposure to enzymes from aggregate breakdown, which would be linked to $[S_x]$ in DAMM in lieu of its current proportionality constant.

Another conceptual model and some empirical data (Six *et al.*, 2002; Stewart *et al.*, 2008) suggest that a soil's C saturation limit could be estimated as functions of soil texture, mineralogy, size class, and management. The fraction of new C inputs sequestered and unavailable for decomposition then could be simulated as a function of the measured saturation deficit. On a related line, Mayes *et al.* (2012) fitted the Langmuir sorption equation, which has a M–M form, to demonstrate that soil order, pH, texture, total organic C, and total Fe oxide content could account for much of the observed variation in maximum DOC sorption capacity (Q_{max}) and the binding coefficient (k). Although entirely based on empirical functions, a module based on these relationships could help determine the fraction of newly input C that becomes unavailable as $[S_x]$ in DAMM, thus linking fast-response respiration processes to soil C stabilization processes.

We speculate that variation in soil C stocks across the globe will be better simulated when ESMs incorporate databases on soil classification, mineralogy, texture, and drainage (e.g., Batjes, 2000; Webb *et al.*, 2000; FAO/IIASA/ISRIC/ISSCAS/JRC, 2012; ISRIC, 2013), rather than using existing model structures and 'spin up'. The use of 'spin up' in ESMs is to generate an equilibrium spatial distribution of soil C based on the small difference between simulated GPP and simulated total ecosystem respiration, which is then apportioned to various soil or ecosystem pools using transfer coefficients. Interestingly, most of the variation in simulated C stocks across ESMs is driven by differences in NPP and the parameterization of soil heterotrophic respiration (Todd-Brown *et al.*, 2013). In contrast, the soil science literature emphasizes the importance of stabilization processes for understanding spatial and temporal variation in soil C stocks (Oades, 1988; Six *et al.*, 2002; Trumbore, 2009). The aggregation and sorption modules envisioned in Fig. 1 could address these stabilization and destabilization processes directly. Scaling parameterization of such modules would be a challenge, to be sure, but no more so than scaling transfer functions among pools in current ecosystem models and ESMs (e.g., Koven *et al.*, 2013).

Freeze–thaw processes

The fraction of C stored in the world's permafrost that will become available for enzymatic degradation as soil temperatures cross the freeze–thaw transition could strongly influence biotic feedbacks to climate change (Harden *et al.*, 2012). In addition, significant wintertime soil respiration at near freezing soil temperatures has been demonstrated (Sommerfeld *et al.*, 1993), with apparent Q_{10} values reported in the 10s or 100s (Mikan *et al.*, 2002; Monson *et al.*, 2006) across a narrow range of temperature just below and above 0 °C. The DAMM model structure offers an opportunity to simulate the effects of the phase transition of soil water.

Tucker (2014) modified the DAMM model for frozen soils by partitioning the volumetric water term (θ) into terms for solid (*ice*) and liquid (θ_{liq}) phases. Diffusion of soluble substrates occurs only in the liquid phase, which increases rapidly and nonlinearly as soils thaw from −2 °C to +1 °C. This increase in θ_{liq} relieves substrate diffusion limitation that was present in the frozen soil, causing the respiration rate to increase much more than would be expected due only to the two degree temperature effect in the Arrhenius equation. This mechanistic simulation of the nonlinear effects of thawing on substrate diffusion provides a mathematical explanation for the very high apparent Q_{10} values measured in this narrow temperature range, while making only a slight modification of the DAMM model to partition soil water into liquid and solid phases. The *ice* term is also included in the calculation of air-filled pore space to account for the addition space occupied by ice compared to liquid water.

Gas transport module and soil depths

The gas diffusivity equation (Fig. 1), based on the air-filled pore spaced raised to the 4/3rds power (Millington, 1959) is the simplest of many that have been described in the literature, but may not be the best (Davidson & Trumbore, 1995; Moyano *et al.*, 2013). In contrast to most applications of a diffusivity constant, where D_{gas} is expressed in units of cm^3 cm^{-1} s^{-1}, it is unitless here because the diffusion distance is not explicitly simulated. A probability distribution function may be a good option for simulating the effect of variation of diffusion distances. The same applies to diffusion distances of solutes in water films. In addition, the model shown in Fig. 1 could be applied to each of several soil horizons, and the diffusion of gases and movement of water between horizons explicitly simulated and compared to measured profiles of soil gas concentrations, including radon to validate diffusivity estimates (Davidson & Trumbore, 1995).

Other types of respiration and other gases

While originally intended for aerobic respiration, the basic DAMM structure is applicable to other respiratory

processes of CO_2, CH_4, and N_2O production and consumption. Because these processes are interlinked through common substrates and the contrasting effects of O_2 as either an essential substrate or a potential inhibitor, the mechanistic simulation of fluxes of any one gas should be consistent with mechanistic simulations and observations of fluxes of the other gases.

To model CH_4 production, the specific substrates for aceticlastic methanogenesis or for autotrophic methanogenesis from H_2 would replace $[S_x]$, O_2 would become an inhibitor rather than a substrate, and Arrhenius functions for the V_{max} and K_m of those enzymes would be applied. Similarly, O_2 is an inhibitor of N_2O production and consumption by being the preferred electron acceptor.

We have done preliminary work to modify the DAMM equation for CH_4 oxidation, keeping the same overall structure, but the substrates, CH_4 and O_2, are both gases, and so only gaseous diffusion is important for substrate supply (Fig. 3). Preliminary analysis shows a good fit with preliminary automated chamber flux data at the Howland Forest of Maine (Fig. 4). Measured uptake rates closely followed variation in soil moisture, with little apparent correspondence with seasonal variation in soil temperature. The best fit was obtained when E_a = 30 kJ mol^{-1} (corresponding to a Q_{10} of about 1.6) and K_m = 7 ppm for CH_4. Because the soil atmospheres have below ambient CH_4 concentrations in these well drained, CH_4-consuming soils $[S_{CH4} \approx 1$ ppm$]$, the M–M part of this equation solves to about $V_{max}/8$ ($\approx [V_{max} \times 1$ ppm$]/[7$ ppm + 1 ppm$]$). Hence, although the Arrhenius function prescribes an E_a of V_{max} with moderate temperature sensitivity, it has a very small effect on simulated fluxes, because the simulated CH_4 oxidation rate is generally only about 1/8th of V_{max}. Instead, most of the temporal variation is related to variation about this '1/8th' term,
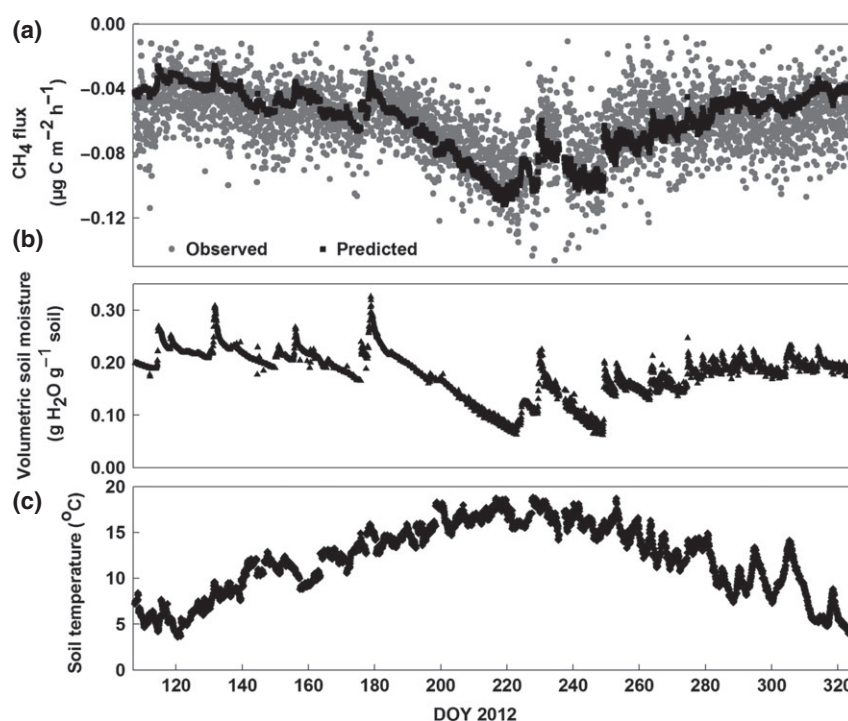
due to changing soil moisture and its effect on substrate diffusion and concentration.

As with aerobic CO_2 flux (Fig. 2a), the temperature–moisture response surface for CH_4 uptake is an emergent property of the linked DAMM equations (Fig. 2b). Consistent with many field observations (Crill *et al.*, 1994; Whalen & Reeburgh, 1996), the model predicts low rates of CH_4 consumption and little apparent temperature sensitivity at high soil water contents, when gaseous diffusion is blocked by water-filled pore spaces, whereas the moderate temperature sensitivity of the prescribed activation energy for CH_4 oxidation is expressed only at low soil moisture contents when substrate diffusion is less limiting (Fig. 2b). Indeed, the temperature–moisture response surface in Fig. 2b that emerges from linking M–M and Arrhenius kinetics with diffusion equations is strikingly similar to an empirically derived response surface for boreal soils (Whalen & Reeburgh, 1996).

Microbial population and enzyme production

Our first application of DAMM indicated that model performance improved if we allowed the pre-exponential factor (α) of the Arrhenius equation for V_{max} to vary seasonally (Davidson *et al.*, 2012). We speculated that variation in α was serving as a proxy for seasonal variation in the enzymatic capacity of the soil, and it could also vary among soil types. This is analogous to how leaf nitrogen (N) concentration is used as a proxy for photosynthetic enzymatic capacity in many canopy models, as originally envisioned by Farquhar *et al.* (1980). Hence, this is an obvious place in the model structure for integration with a module that simulates microbial and enzymatic dynamics, including C–N interactions and microbial carbon use efficiency.

For example, the Microbial Carbon and Nitrogen Physiology (MCNiP) model (Drake *et al.*, 2013), following an emerging family of microbial enzyme models (Schimel & Weintraub, 2003; Allison *et al.*, 2010; Wieder *et al.*, 2013, 2014), uses inputs of DOC and DON from exoenzyme activity to simulate microbial C and N uptake and allocation. A modified diagram of the model shows how it could interface with DAMM (Fig. 5). Once taken up, C and N are partitioned between exoenzyme synthesis and microbial growth, which determines α in DAMM. The growth of the microbial biomass pool can be C or N limited, depending upon which resource is less available. Any C and N taken up in excess of enzyme production and growth is mineralized, which is called overflow metabolism in the case of C and net mineralization in the case of N. Integration of a model like MCNiP into DAMM would also separate the steps of enzymatic deploymerization

$$\text{Airfilledporosity} = 1 - \frac{BD}{PD} - \Theta$$

$$[CH_4] = D_{CH4} \times \frac{1.8uLCH_4}{Lair} \times a^{4/3} \qquad [O_2] = D_{O2} \times \frac{0.2LO_2}{Lair} \times a^{4/3}$$

$$R_{CH4} = Vmax_{CH4} \times \frac{[CH_4]}{kM_{CH4} + [CH_4]} \times \frac{[O_2]}{kM_{O2} + [O_2]}$$

$$kM_{O2} = \alpha_{kMO2} \times e^{-EakMO2/RT}$$

$$kM_{CH4} = \alpha_{kMCH4} \times e^{-EakMCH4/RT}$$

$$Vmax_{CH4} = \alpha_{VmaxCH4} \times e^{-EaVmaxCH4/RT}$$

Fig. 3 Schematic diagram of the DAMM model revised for simulating CH_4 oxidation.

Fig. 4 Preliminary data from the Howland Forest in central Maine for (a) methane fluxes measured by automated chambers (gray points); (b) soil moisture at 10 cm depth; and (c) soil temperature at 10 cm depth. Predicted CH_4 fluxes, shown in black points in top panel, are from application of the DAMM model as described in the text. Unpublished data from Davidson and Savage.
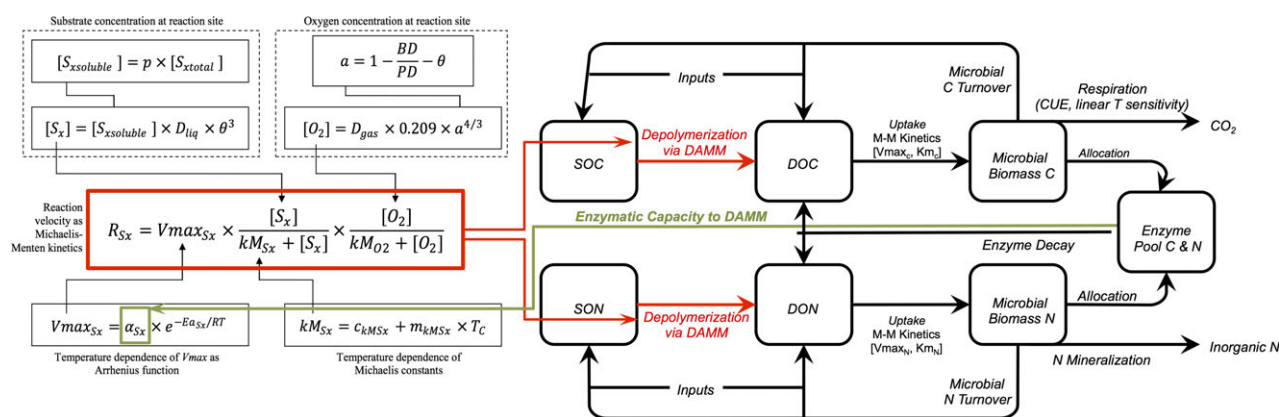
Fig. 5 Schematic diagram of the Microbial Carbon and Nitrogen Physiology (MCNiP) model, revised from Drake *et al.* (2013) with linkages to the DAMM model Red arrows show how output from DAMM will inform MCNiP; the green arrow shows how output from MCNiP will inform DAMM.

of SOM and microbial uptake of DOC. The advantages of simulating a dynamic DOC pool was already discussed above with respect to wet-up events and rhizosphere inputs.

The MCNiP model currently simulates microbial biomass and enzyme production generically, without distinguishing among microbial and exoenzyme functional group models. Additional complexity could be added by distinguishing between microbial functional groups, such as saprotrophic fungi, mycorrhizal fungi, and bacteria, and the impacts of their differences in abundance, activity, turnover rate, and stoichiometry (Allison, 2012; Waring *et al.*, 2013).

Adding microbial processes such as these is probably an excellent example of the advantage of using a modular approach, where the importance of model

assumption in this rapidly changing field could be assessed. For example, Wieder *et al.* (2014) proposed that the K_m for enzymatic reactions could be varied depending upon whether the substrate is sorbed onto mineral surfaces. While our preference would be to separate sorption/desorption process simulation from the simulation of enzyme affinity for a substrate at its reaction site, combining these two processes into a single but widely varying K_m parameter could be a clever shortcut, but it would useful to compare the two approaches using a common modeling framework.

Scaling microbial processes is inherently challenging, but lessons can be learned from scaling gross primary productivity (Williams *et al.*, 1997; Manzoni & Porporato, 2009; Todd-Brown *et al.*, 2012), where results of fine scale models were aggregated and equations simplified going from small to large spatial and temporal scales. The process-level functions represented in DAMM and our vision for its modular expansion are not fundamentally different from similar functions that are being scaled for simulation of CO_2, CH_4, and N_2O fluxes in more highly parameterized ESMs (e.g., Zaehle & Friend, 2010; ; Riley *et al.*, 2011). Model structures must consider climate, soil, and vegetation datasets available at larges scales as input data for variables and parameters.

Managing complexity and parsimony with modular additions

Managing modular growth of a model is, itself, a developing science. For example, the Predictive Ecosystem Analyzer (PEcAn, www.pecanproject.org) is an open-source scientific workflow system and ecoinformatics toolbox that manages the circulation of information in and out of models, facilitates formal data assimilation using a fully Bayesian approach to parameter estimation, and automates a number of model analyses that allow the system to partition and ascribe uncertainties to different model parameters and processes (LeBauer *et al.*, 2013). There are a number of advantages to this statistical approach, but the most important are the ability to: (1) utilize data regardless of the spatial and temporal scale over which it was collected; (2) use the model to identify new field experiments or sampling campaigns (i.e., collecting data on the most poorly constrained processes); (3) estimate parameters directly from data; and (4) use objective evaluation functions to determine whether one model structure is better than another given the available data.

As the model becomes more complicated, with unintended redundancies among modules, sophisticated analytical tools can enable model simplification (i.e., combing similar terms), extract the model's critical components, and thus 'cut away model fat.' Simplifying the model not only reduces computational time (Riley, 2013), but also highlights key processes that should be kept in the descendent, more modularized model.

Conclusion

As we develop numerical models to test and to apply our understanding of biotic feedbacks to climate change, land use change, and changing nutrient cycles, we cannot avoid complexity, because many of the interacting biotic responses are inherently complex. That said, a way forward, demonstrated in related disciplines, is to start with a core understanding of biotic reaction processes and then add complexity as knowledge, data, computing power, and skill permit. The relatively simple linking of Arrhenius and Michaelis–Menten kinetics already produces emergent properties of response functions for both leaf photosynthesis and soil respiration to environmental drivers, allowing mathematical expression of both substrate supply and temperature to yield new insight into the critical importance of their interacting effects. The spatial and temporal heterogeneity of many physical, chemical, and biological processes related to substrate supply, SOM stabilization, and enzyme production will require additional equations, which can be added modularly to improve model performance and to glean further insight. This vision for linking soil C cycling processes offers a means of conceptually and numerically linking our understanding of fast-response processes of soil gas exchange with longer-term dynamics of soil C and N stocks.

References

Allison SD (2012) A trait-based approach for modelling microbial litter decomposition. *Ecology Letters*, **15**, 1058–1070.

Allison SD, Wallenstein MD, Bradford MA (2010) Soil-carbon response to warming dependent on microbial physiology. *Nature Geoscience*, **3**, 336–340.

Arrhenius S (1889) Uber die reaktionsgeschwindigkeit bei der inversion von rohrzucker durch sauren. *Zeitschrift für Physikalische Chemie*, **4**, 226–248.

Baldocchi D, Meyers T (1998) On using eco-physiological, micrometeorological and biogeochemical theory to evaluate carbon dioxide, water vapor and trace gas fluxes over vegetation: a perspective. *Agricultural and Forest Meteorology*, **90**, 1–25.

Batjes NH (2000) *Global Data Set of Derived Soil Properties, 0.5-Degree Grid, International Soil Reference and Information Centre – World Inventory of Soil Emission Potentials*. Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, TN, USA. Available at: http://www.daac.ornl.gov. doi:10.3334/ORNLDAAC/546 (accessed 8 September 2014).

Crill P, Martikainen PJ, Nykanen H, Silvola J (1994) Temperature and N fertilization effects on methane oxidation in a drained peatland soil. *Soil Biology and Biochemistry*, **26**, 1331–1339.

Davidson EA, Janssens I (2006) Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature*, **440**, 165–173.

Davidson EA, Trumbore SE (1995) Gas diffusivity and production of CO_2 in deep soils of the eastern Amazon. *Tellus B*, **47**, 550–565.

Davidson EA, Belk E, Boone RD (1998) Soil water content and temperature as independent or confounded factors controlling soil respiration in a temperate mixed hardwood forest. *Global Change Biology*, **4**, 217–227.

Davidson EA, Verchot LV, Cattanio JH, Ackerman IL, Carvalho JEM (2000) Effects of soil water content on soil respiration in forests and cattle pastures of eastern Amazonia. *Biogeochemistry*, **48**, 53–69.

Davidson EA, Janssens IA, Luo Y (2006) On the variability of respiration in terrestrial ecosystems: moving beyond Q10. *Global Change Biology*, **12**, 154–164.

Davidson EA, Samanta S, Caramori SS, Savage K (2012) The Dual Arrhenius and Michaelis-Menten kinetics model for decomposition of soil organic matter at hourly to seasonal time scales. *Global Change Biology*, **18**, 371–384.

Drake JE, Darby BA, Giasson MA et al. (2013) Stoichiometry constrains microbial response to root exudation insights from a model and a field experiment in a temperate forest. *Biogeosciences*, **10**, 821–838.

FAO/IIASA/ISRIC/ISSCAS/JRC (2012) *Harmonized World Soil Database (version 1.2)*. FAO, Rome, Italy; IIASA, Laxenburg, Austria.

Farquhar GD, von Caemmerer S, Berry JA (1980) A biochemical model of photosynthetic CO_2 assimilation in leaves of C3 species. *Planta*, **149**, 78–90.

Galwey AK, Brown ME (1995) A theoretical justification for the application of the Arrhenius equation to kinetics of solid state reactions (mainly ionic crystals). *Proceedings of the Royal Society A*, **450**, 501–512.

German DP, Marcelo KRB, Stone MM, Allison SD (2012) The Michaelis-Menten kinetics of soil extracellular enzymes in response to temperature: a cross-latitudinal study. *Global Change Biology*, **18**, 1468–1479.

Gill R, Jackson RB (2003) *Global Distribution of Root Turnover in Terrestrial Ecosystems*. Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, TN, USA. doi:10.3334/ORNLDAAC/661. Available at: http://www.daac.ornl.gov (accessed 8 September 2014).

Harden JW, Koven CD, Ping CL et al. (2012) Field information links permafrost carbon to physical vulnerabilities of thawing. *Geophysical Research Letters*, **39**, L15704. doi:10.1029/2012GL051958.

Hedges JI, Eglinton G, Hatcher PG et al. (2000) The molecularly-uncharacterized component of nonliving organic matter in natural environments. *Organic Geochemistry*, **31**, 945–958.

Hochachka PW, Somero GN (2002) *Biochemical Adaptation: Mechanism and Process in Physiological Evolution*. Oxford University Press, New York, NY.

ISRIC – World Soil Information (2013) SoilGrids: an automated system for global soil mapping. Available at: http://soilgrids1 km.isric.org (accessed 8 September 2014).

Jackson RB, Mooney HA, Schulze E-D (2003) *Global Distribution of Fine Root Biomass in Terrestrial Ecosystems*. Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, TN, USA. doi:10.3334/ORNLDAAC/658. Available at: http://www.daac.ornl.gov (accessed 8 September 2014).

Jenkinson DS, Adams DE, Wild A (1991) Model estimates of CO_2 emissions from soil in response to global warming. *Nature*, **351**, 304–306.

Keenan TF, Davidson EA, Moffat AM et al. (2012) Using model-data fusion to interpret past trends, and quantify uncertainties in future projections, of terrestrial ecosystem carbon cycling. *Global Change Biology*, **18**, 1971–1987.

Keenan TF, Davidson EA, Munger JW, Richardson AD (2013) Rate my data: quantifying the value of ecological data for the development of models of the terrestrial carbon cycle. *Ecological Applications*, **23**, 273–286.

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

Koven CD, Riley WJ, Subin ZM et al. (2013) The effect of vertically-resolved soil biogeochemistry and alternate soil C and N models on C dynamics of CLM4. *Biogeosciences*, **10**, 7109–7131.

Laidler KJ, King MC (1983) The development of transition-state theory. *Journal of Physical Chemistry*, **87**, 2657–2664.

LeBauer DS, Wang D, Richter KT, Davidson CC, Dietze MC (2013) Facilitating feedbacks between field measurements and ecosystem models. *Ecological Monographs*, **83**, 133–154.

Linn D, Doran J (1984) Effect of water-filled pore-space on carbon-dioxide and nitrous-oxide production in tilled and nontilled soils. *Soil Science Society of America Journal*, **48**, 1267–1272.

Manzoni S, Porporato A (2009) Soil carbon and nitrogen mineralization: theory and models across scales. *Soil Biology and Biochemistry*, **41**, 1355–1379.

Mayes MA, Heal KR, Brandt CC et al. (2012) Relation between soil order and sorption of dissolved organic carbon in temperate subsoils. *Soil Science Society of America Journal*, **76**, 1027–1037.

Michaelis L, Menten ML (1913) Die kinetik der invertin wirkung. *Biochemische Zeitschrift*, **49**, 334–336.

Mikan CJ, Schimel JP, Doyle AP (2002) Temperature controls of microbial respiration in arctic tundra soils above and below freezing. *Soil Biology and Biochemistry*, **34**, 1785–1795.

Millington RJ (1959) Gas diffusion in porous media. *Science*, **130**, 100–102.

Monod J (1949) The growth of bacterial cultures. *Annual Review of Microbiology*, **3**, 371–394.

Monson RK, Lipson DL, Burns SP et al. (2006) Winter forest soil respiration controlled by climate and microbial community composition. *Nature*, **439**, 711–714.

Moyano FE, Manzoni S, Chenu C (2013) Responses of soil heterotrophic respiration to moisture availability: an exploration of processes and models. *Soil Biology and Biochemistry*, **59**, 72–85.

Oades JM (1988) The retention of organic matter in soils. *Biogeochemistry*, **5**, 35–70.

Oikawa PY, Grantz DA, Chatterjee A et al. (2014) Unifying soil respiration pulses, inhibition, and temperature hysteresis through dynamics of labile soil carbon and O_2. *Journal of Geophysical Research: Biogeoscience*, **119**, 521–536.

Parton W, Schimel D, Cole C, Ojima D (1987) Analysis of factors controlling soil organic matter levels in Great Plains grasslands. *Soil Science Society of America Journal*, **51**, 1173–1179.

Raich JW, Schlesinger WH (1992) The global carbon-dioxide flux in soil respiration and its relationship to vegetation and climate. *Tellus B*, **44**, 81–99.

Riley WJ (2013) Using model reduction to predict the soil-surface C18OO flux: an example of representing complex biogeochemical dynamics in a computationally efficient manner. *Geoscientific Model Development*, **6**, 345–352.

Riley WJ, Subin ZM, Lawrence DM et al. (2011) Barriers to predicting changes in global terrestrial methane fluxes: analyses using CLM4Me, a methane biogeochemistry model integrated in CESM. *Biogeosciences*, **8**, 1925–1953.

Savage KE, Davidson EA, Richardson A, Hollinger DY (2009) Three scales of temporal resolution from automated soil respiration. *Agricultural and Forest Meteorology*, **149**, 2012–2021.

Schenk HJ, Jackson RB (2002) Global biogeography of roots. *Ecological Monographs*, **72**, 311–328.

Schenk HJ, Jackson RB (2003) Global Distribution of Root Profiles in Terrestrial Ecosystems. Oak Ridge National Laboratory Distributed Active archive Center, Oak Ridge, TN, USA. doi:10.3334/ORNLDAAC/660. Available at: http://www.daac.ornl.gov (accessed 8 September 2014).

Schimel JP, Weintraub MN (2003) The implications of exoenzyme activity on microbial carbon and nitrogen limitation in soil: a theoretical model. *Soil Biology and Biochemistry*, **35**, 549–563.

Schlesinger WH (1977) Carbon balance in terrestrial detritus. *Annual Review of Ecology and Systematics*, **8**, 51–81.

Schmidt MWI, Torn MS, Abiven S et al. (2011) Persistence of soil organic matter as an ecosystem property. *Nature*, **478**, 49–56.

Segoli M, De Gryze S, Dou F et al. (2013) AggModel: a soil organic matter model with measurable pools for use in incubation studies. *Ecological Modeling*, **263**, 1–9.

Sellers PJ, Dickinson RE, Randall DA et al. (1997) Modeling the exchanges of energy, water, and carbon between continents and the atmosphere. *Science*, **275**, 502–509.

Six J, Paustian K (2014) Aggregate-associated soil organic matter as an ecosystem property and a measurement tool. *Soil Biology and Biochemistry*, **68**, A4–A9.

Six J, Conant RT, Paul EA, Paustian K (2002) Stabilization mechanisms of soil organic matter: implications for C-saturation of soils. *Plant and Soil*, **241**, 155–176.

Sollins P, Homann P, Caldwell BA (1996) Stabilization and destabilization of soil organic matter: mechanisms and controls. *Geoderma*, **74**, 65–105.

Sollins P, Swanston C, Kramer M (2007) Stabilization and destabilization of soil organic matter—a new focus. *Biogeochemistry*, **85**, 1–7.

Sommerfeld RA, Mosier AR, Musselman RC (1993) CO_2, CH_4 and N_2O flux through a Wyoming snowpack and implications for global budgets. *Nature*, **361**, 140–142.

Sorensen R, Novak N (1996) The use of Michaelis-Menten kinetics in cell biology and physiology teaching laboratories. *Biochemical Education*, **24**, 26–28.

Stewart CE, Paustian K, Conant RT et al. (2008) Soil carbon saturation: evaluation and corroboration by long-term incubations. *Soil Biology and Biochemistry*, **40**, 1741–1750.

Stone MM, Weiss MS, Goodale CL *et al.* (2012) Temperature sensitivity of soil enzyme kinetics under N-fertilization in two temperate forests. *Global Change Biology*, **18**, 1173–1184.

Todd-Brown KEO, Hopkins FM, Kivlin SN, Talbot JM, Allison SD (2012) A framework for representing microbial decomposition in coupled climate models. *Biogeochemistry*, **109**, 19–33.

Todd-Brown KEO, Randerson JT, Post WM, Hoffman FM, Tarnocai C, Schuur EAG, Allison SD (2013) Causes of variation in soil carbon simulations from 5 CMIP5 Earth system models and comparison with observations. *Biogeosciences*, **10**, 1717–1736.

Trumbore SE (2009) Radiocarbon and soil carbon dynamics. *Annual Review of Earth and Planetary Sciences*, **37**, 47–66.

Tucker CL (2014) Reduction of air- and liquid water-filled soil pore space with freezing explains high temperature sensitivity of soil respiration below 0°C. *Soil Biology and Biochemistry*, **78**, 90–96.

Wang G, Post WM, Mayes MA *et al.* (2013) Parameter estimation for models of ligninolytic and cellulolytic enzyme kinetics. *Soil Biology and Biochemistry*, **48**, 28–38.

Waring BG, Averill C, Hawkes CV (2013) Differences in fungal and bacterial physiology alter soil carbon and nitrogen cycling: insights from meta-analysis and theoretical models. *Ecology Letters*, **16**, 887–894.

Webb RW, Rosenzweig CE, Levine ER (2000) *Global Soil Texture and Derived Waterholding Capacities*. Oak Ridge National Laboratory Distributed Active Archive Center, Oak Ridge, TN, USA. Available at: http://www.daac.ornl.gov. doi:10.3334/ORNLDAAC/548 (accessed 8 September 2014).

Whalen SC, Reeburgh WS (1996) Moisture and temperature sensitivity of CH_4 oxidation in boreal soils. *Soil Biology and Biochemistry*, **28**, 1271–1281.

Wieder WR, Bonan GB, Allison SD (2013) Global soil carbon projections are improved by modelling microbial processes. *Nature Climate Change*, **3**, 909–912.

Wieder WR, Grandy AS, Kallenbach CM, Bonan GB (2014) Integrating microbial physiology and physiochemical principles in soils with the MIcrobial-MIneral Carbon Stabilization (MIMICS) model. *Biogeosciences Discussions*, **11**, 1147–1185.

Williams M, Rastetter EB, Fernandes DN, Goulden ML, Shaver GR, Johnson LC (1997) Predicting gross primary productivity in terrestrial ecosystems. *Ecological Applications*, **7**, 882–894.

Woodwell GM (1983) Biotic effects on the concentration of atmospheric carbon dioxide; a review and projection. In: *Changing Climate* (eds Nierenberg WA , Brewer PG, Machta L, Nordhaus WD, Revelle RR, Schelling TC, Smagorinsky J, Waggoner PB, Woodwell GM), pp. 216–241. NAS Press, Washington, DC.

Zaehle S, Friend AD (2010) Carbon and nitrogen cycle dynamics in the O-CN land surface model: 1. Model description, site-scale evaluation and sensitivity to parameter estimates. *Global Biogeochemical Cycles*, **24**, GB1005.