

## Soil Carbon Storage Response to Temperature: an Hypothesis

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Recently, global and some regional observations of soil carbon stocks and turnover times have implied that warming may not deplete soil carbon as much as predicted by ecosystem models. The proposed explanation is that microbial respiration of carbon in 'old' mineral pools is accelerated less by warming than ecosystem models currently assume. Data on the sensitivity of soil respiration to temperature are currently conflicting. An alternative or additional explanation is that warming increases the rate of physico-chemical processes which transfer organic carbon to 'protected', more stable, soil carbon pools. These processes include adsorption reactions, some of which are known to have positive activation energies. Theoretically, physico-chemical reactions may be expected to respond more to warming than enzyme-mediated microbial reactions. A simple analytical model and a complex multi-pool soil carbon model are presented, which separate transfers between pools due to physico-chemical reactions from those associated with microbial respiration. In the short-term, warming depletes soil carbon. But in the long-term, carbon losses by accelerated microbial respiration are offset by increases in carbon input to the soil (net production) and any acceleration of soil physico-chemical 'stabilization' reactions. In the models, if net production rates are increased in response to notional warming by a factor of 1.3, and microbial respiration (in all pools) by 1.5, then soil carbon at equilibrium remains unchanged if physico-chemical reactions are accelerated by a factor of about 2.2 (50 % more than microbial reactions). Equilibrium soil carbon increases if physico-chemical reactions are over 50 % more sensitive to warming than soil respiration.

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**Key words:** Soil organic matter, carbon, respiration, temperature, stabilization, decomposition, model.

### INTRODUCTION

The response of soils to increasing temperature is an important issue. Currently, total net primary productivity ( $P_n$ ) of global land vegetation is thought to exceed total heterotrophic (litter and soil) respiration, owing to  $\text{CO}_2$ , N and climate enhancements of  $P_n$ . About 2 Gt C per year is being removed from the atmosphere and stored in vegetation and soil, slowing the rate of global warming (Bolin *et al.*, 2000; Lenton, 2000). Currently, all of the major dynamic global vegetation models predict that heterotrophic respiration (commonly referred to as soil respiration) will increase more than  $P_n$  in response to warming alone. Consequently, the terrestrial carbon sink is predicted to weaken or collapse towards the end of this century, assuming business-as-usual greenhouse gas emissions (Cox *et al.*, 2000; White *et al.*, 2000; Cramer *et al.*, 2001). If soil respiration increased less steeply with temperature, the terrestrial sink would persist longer, potentially until net photosynthesis saturated at high  $\text{CO}_2$  levels (Cao and Woodward, 1998).

Recently, it has been suggested that soil carbon pools may be depleted much less than predicted by most ecosystem models. The basic evidence is that, in some parts of the world, there are no clear trends of decreasing soil carbon with increasing mean annual temperature. The plant-soil ecosystem contains conflicting mechanisms: soil

carbon may be increased by increasing  $P_n$ , possibly due to better water and nutrient availability, or decreased by increasing respiration. Notably, Liski and Westman (1997) found no marked decrease in forest soil carbon along gradients of mean annual temperature in Finland of  $-1$  to  $4^\circ\text{C}$  (Liski *et al.*, 1999). Such trends do exist across the American Great Plains, but these may be explained by trends in  $P_n$  (Jenny, 1980; Burke *et al.*, 1989). Re-examining the global patterns of soil carbon (Post *et al.*, 1982, 1985), Kirschbaum (2000) found a clear trend of decreasing carbon with mean annual temperature for very dry and very wet biomes (with extreme ratios of potential evapotranspiration to precipitation, PET/P). Surprisingly, there was no consistent trend for biomes with PET/P in the range 0.25 to 2.0—encompassing most of the world's vegetation (Fig. 1).

#### *One explanation for insensitivity of soil carbon stocks to temperature*

Currently, the primary explanation for the above observations is that the temperature sensitivity of soil respiration has been over-estimated. The arguments are two-fold.

First, measurements of soil decomposition responses to temperature may be biased towards litter and non-mineral organic matter. Certainly, this bias applies to all litter mass-loss experiments (e.g. Berg *et al.*, 1996), measurements of surface soil  $^{13}\text{C}$  depletion (Bird *et al.*, 1996),  $^{14}\text{C}$  signature in the 'light fraction' (Trumbore *et al.*, 1996) and to some

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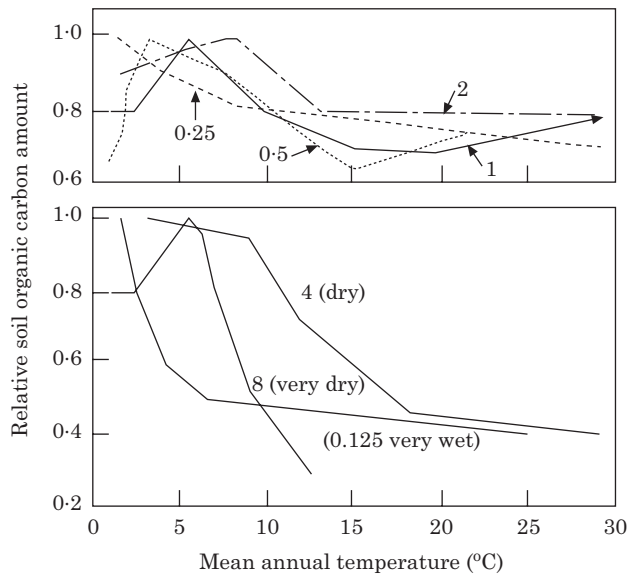


FIG. 1. Relative amounts of soil organic carbon in global biomes with different ratios of potential evapotranspiration to precipitation (PET/P: 8 = dry; 0.125 = wet) expressed as ratios of the highest amounts in each PET/P class. Figure redrawn from Kirschbaum (2000), based on data from Post *et al.* (1982, 1985).

laboratory incubation experiments (see Kirschbaum, 2000). Temperature dependencies in the Century and Rothamsted models (Parton *et al.*, 1987; Jenkinson *et al.*, 1991) equate to  $Q_{10}$  values of about 2 at 30–35 °C, increasing to 4–6 at 5–10 °C—similar to those derived by Kirschbaum (1995) using data from laboratory incubations of litter and soil. In most environments, these temperature dependencies for soil organic matter decomposition, which decreases soil carbon, greatly exceed those observed or predicted for  $P_n$  (Kirschbaum, 2000; Rustad *et al.*, 2000), which increases soil carbon. Some measurements can also be criticized as being short term, possibly observing a transient loss of readily metabolizable carbon. Jarvis and Linder (2000) found that, after 5 years, there was no effect of a 5 °C warming on soil CO<sub>2</sub> efflux from forest plots in Sweden. Additionally, it may be questioned whether seasonal changes in soil CO<sub>2</sub> efflux in the field can be used to derive soil temperature response functions, as there are so many confounding factors (Lloyd and Taylor, 1994; Boone *et al.*, 1998).

Second, some measurements of ‘mineral’ soil respiration suggest a lower temperature sensitivity. Mineral soil occurs below the litter and organic layer, where soil carbon is closely associated with mineral particles—accounting for over 60 % of the carbon in most forest soils. Liski *et al.* (1999) and Giardina and Ryan (2000) proposed that the decomposition/respiration rate of mineral soil carbon is relatively insensitive to temperature. The evidence put forward is that (1) changes in mineral soil <sup>13</sup>C/<sup>12</sup>C ratios that occur when C<sub>3</sub> vegetation is replaced by C<sub>4</sub> vegetation reveal no differences in turnover times that are related to mean annual temperature; and (2) mineral soils incubated at relatively higher temperatures can contain more carbon after 1 year than those incubated at relatively lower

temperatures (Giardina and Ryan, 2000). Also, it is known that the respiration rates of many soils are strongly correlated with the amount of carbon *not* intimately associated with minerals (the ‘light fraction’; Janzen *et al.*, 1992).

However, there is currently no agreed explanation for the Giardina and Ryan (2000) data, which are in conflict with the soil CO<sub>2</sub> efflux data reviewed by Lloyd and Taylor (1994) and the soil incubation data reviewed by Kirschbaum (2000).

#### An alternative explanation

In this paper, an alternative or additional hypothesis is proposed to explain the apparent insensitivity of soil carbon stocks to temperature, under some circumstances. The hypothesis is that warming may increase the rate of physico-chemical processes which transfer organic carbon to ‘protected’, more stable, soil carbon pools. Indeed, physico-chemical ‘stabilization’ reactions may respond more to warming than microbial ‘decomposition/respiration’ reactions. If this were true, soil carbon stocks may remain relatively unchanged, or even increase, with increase in temperature, without invoking low temperature sensitivity for microbial respiration in the older mineral pools.

### SOIL BIOLOGICAL AND PHYSICO-CHEMICAL PROCESSES

Although, in reality, soils consist of a continuum of organic matter in different states (Carpenter, 1981) and a hierarchy of aggregates which may change from being stable to unstable (Golchin *et al.*, 1994), there are considerable difficulties in moving away from the traditional pool-based modelling approach, even though the pools do not correspond to experimentally verifiable fractions (Cambardella, 1997).

Accepting this, models must include one or more ‘slow’ pools, representing organic matter that has been ‘stabilized’ by one of three mechanisms: (1) physical protection in soil aggregates; (2) chemical bonding on to minerals; and (3) chemical recalcitrance. Chemical recalcitrance may be important in the slowest turnover ‘stable’ pools (which contribute little to soil dynamics) and possibly at high latitudes, where lignin can incorporate nitrogen to form condensation products leading to the build-up of thick layers of non-peat humus (Stevenson, 1982; Fog, 1988). However, in most soils, physico-chemical processes are important for stabilization. Negatively charged polysaccharide polymers are strongly adsorbed on to clay surfaces, building microaggregates, and aggregation of mineral particles around organic fragments can cause over 90 % of the pore space to be too small for microbes to pass through (e.g. van Veen and Kuikman, 1990; Oades and Waters, 1991; Jastrow and Miller, 1997).

Some of the mechanisms by which organic matter is stabilized, including the three listed above, may be enzyme-dependent, and linked to microbial activity and respiration; these processes may leave more lignin and alkyl structures

and provide mucilages and metabolites to stabilize aggregates. Consequently, most models couple carbon transfer between pools with respiration (Ågren and Bosatta, 1998).

But some of the stabilization processes are non-biological, involving physico-chemical processes. In the Rothamsted and Century soil models and their derivatives, these processes are normally represented implicitly, by making transfer processes a function of soil clay content (Parton *et al.*, 1987; Jenkinson, 1990; Verberne *et al.*, 1990). More recently, Hassink and Whitmore (1997) proposed a model in which transfers between unprotected and protected pools were represented explicitly using adsorption-desorption kinetics. Thornley (1998, eqn 5.7e) described the transfer to stabilized pools as a function of temperature and the chemical activity of soil water.

This paper goes a step further by proposing that the temperature response functions for microbial respiration reactions and physico-chemical ‘stabilization’ reactions are different. We make two assumptions. First, some soil physico-chemical stabilization involves reactions that require activation energy ( $E_a$ ) and so are accelerated by warming. There are many bonding reactions (Theng, 1974; Burchill *et al.*, 1981; Schulten and Leinweber, 2000). Positive activation energies have been measured for the adsorption of a number of simple molecules on to mineral particles (Table 1). Larger molecules may be expected to have larger activation energies. Warming (to an optimum) may accelerate diffusion and increase the number of adsorption sites (Moreale and van Bladel, 1976). However, it is also true that warming can accelerate desorption; thus fast desorption of organic micro-pollutants can have activation energies of 10–50 kJ mol<sup>-1</sup> (Hulscher and Cornelissen, 1996). We assume that, overall, the balance of physico-chemical processes involved in the stabilization and destabilization of organic matter is enhanced by warming. Second, soil physico-chemical reactions leading to stabilization may be more temperature sensitive than microbial respiration reactions. The latter may be expected to have relatively low activation energies, because they are facilitated by enzymes—which function by enabling more molecules to react at low temperatures, lowering  $E_a$ . Reactions with low  $E_a$  have low  $Q_{10}$  values; that is, they are relatively less sensitive to temperature—essentially because they occur relatively rapidly anyway. It can be shown that  $Q_{10} = \exp(10E_a/RT^2)$ , where  $R$  is the gas constant and  $T$  is a common reference temperature for Arrhenius and  $Q_{10}$  equations (Thornley and Johnson, 2000, eqn 5.1). At 10 °C,  $Q_{10}$ s of 1.5 and 2 for soil respiration correspond to activation energies,  $E_a$ , of 27 and 46 kJ mol<sup>-1</sup>. This is similar to the activation energies given in Table 1, but may be less than those for the net adsorption of large molecules.

## MODELS SEPARATING BIOLOGICAL AND PHYSICO-CHEMICAL PROCESSES

### Simple analytical model

Consider a simple soil organic matter model in which the rate constants for microbial respiration and

TABLE 1. Examples of activation energies for adsorption of chemical species in soils

Adsorption reactions	Activation energy (kJ mol <sup>-1</sup> )	Reference
Isocil on illite and silica gel	0–25	Lindstrom <i>et al.</i> (1970)
Phosphate on calcite	30	Griffin and Jurinak (1974)
FeEDDHA in calcareous soil	39–62	Jorda <i>et al.</i> (1992)
Zinc in calcareous soil	5–17	Ma and Liu (1997)

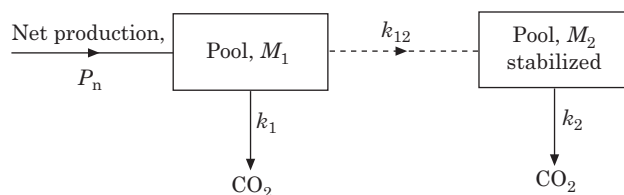


FIG. 2. A simple two-pool soil organic carbon model.  $k$  indicates a rate constant (d<sup>-1</sup>).  $k_1$  and  $k_2$  represent the microbiological ‘decomposition’ processes (respiration and mineralization);  $k_{12}$  represents the physico-chemical ‘stabilization’ processes leading to protection of soil organic matter from decomposition. Microbial processes are shown with solid lines, physico-chemical processes with broken lines.

physico-chemical processes are separated (Fig. 2). This model is not a realistic representation of soil processes, but rather serves to demonstrate the effects of warming on soil carbon when physico-chemical stabilization reactions are assumed to be more temperature sensitive than microbial respiration of unstabilized carbon. The model has the merit of being analytically soluble. The parameter values used below are illustrative and all processes are assumed to be linear with constant rate constants. [The ICBM model (Andrén and Kätterer, 1997) is a two-pool soil model of identical structure to Fig. 2 and with equivalent mathematical solutions; the model is of great heuristic value for addressing simple soil problems, although temperature responses are not considered.]

Net primary production,  $P_n$  (0.005 kg C m<sup>-2</sup> d<sup>-1</sup>), equal to total above- and below-ground litter, provides a flux into carbon pool,  $M_1$  (0.9804 kg C m<sup>-2</sup> at equilibrium). Linear rate constant  $k_1$  (0.005 d<sup>-1</sup>) represents microbial respiration of this pool, giving a turnover time of 200 d ( $1/k_1$ ) with loss of carbon as CO<sub>2</sub>. Rate constant  $k_2$  (0.00001 d<sup>-1</sup>) represents microbial respiration of the second ‘stabilized’ pool of organic carbon ( $M_2 = 9.804$  kg C m<sup>-2</sup> at equilibrium). Physico-chemical conversion of carbon from  $M_1$  to  $M_2$ , without efflux of CO<sub>2</sub>, is given an intermediate rate constant  $k_{12}$  (0.0001 d<sup>-1</sup>). That is, the rate constant for physico-chemical stabilization reactions is assumed to be 50-times less than that for microbial respiration/decomposition of the first pool but ten-times greater than that of the stabilized pool. The initial values of the two state variables,

TABLE 2. Effects of increasing the rate constants (notionally in response to warming) for microbial respiration reactions ( $k_1$  and  $k_2$ ), physico-chemical 'stabilization' reactions ( $k_{12}$ ) and net primary production ( $P_n$ ) on the total amount of soil organic carbon at equilibrium [ $M(\infty)$ , kg C m<sup>-2</sup>] predicted by the model in Fig. 2 [eqn (4)]

Scenarios (see text)	Net production $P_n$ (kg C m <sup>-2</sup> d <sup>-1</sup> )	Microbial respiration reactions $k_1$ and $k_2$ (d <sup>-1</sup> )	Physico-chemical reactions $k_{12}$ (d <sup>-1</sup> )	Total equilibrium soil carbon $M(\infty)$ (kg C m <sup>-2</sup> )
(a)	1	1	1	10.8
(b)	2	2	2	10.8
(c)	1	2	1	3.0
(d)	1	2	2	5.4
(e)	1	2	3	7.8
(f)	1	2	4	10.1
(g)	2	2	4	20.2

1 = standard illustrative values,  $P_n = 0.005$  kg C m<sup>-2</sup> d<sup>-1</sup>,  $k_1 = 0.005$  d<sup>-1</sup>,  $k_2 = 0.00001$  d<sup>-1</sup>,  $k_{12} = 0.0001$  d<sup>-1</sup>; 2 = double the standard values; 3 = treble the standard values; 4 = four-times the standard values.

$M_1$  and  $M_2$ , are equal to their equilibrium values [eqn (4)]. The differential equations defining this model are:

$$\begin{aligned}\frac{dM_1}{dt} &= P_n - (k_{12} + k_1)M_1 \\ \frac{dM_2}{dt} &= k_{12}M_1 - k_2M_2\end{aligned}\quad (1)$$

and the respiratory flux,  $R$  (kg C m<sup>-2</sup> d<sup>-1</sup>), is

$$R = k_1M_1 + k_2M_2 \quad (2)$$

Equation (1) can be solved analytically to give:

$$\begin{aligned}M_1 &= \frac{1}{k_1 + k_{12}} [P_n - \{P_n - (k_1 + k_{12})M_1(0)\}e^{-(k_1 + k_{12})t}] \\ M_2 &= M_2(0)e^{-k_2t} + \frac{k_{12}}{k_1 + k_{12}} \\ &\times \left[ \frac{P_n}{k_2} (1 - e^{-k_2t}) + \frac{P_n - (k_1 + k_{12})M_1(0)}{k_1 + k_{12} - k_2} \right. \\ &\times \left. (e^{-(k_1 + k_{12})t} - e^{-k_2t}) \right] \quad (3)\end{aligned}$$

The equilibrium or steady-state values of  $M_1$ ,  $M_2$ , total soil carbon,  $M = M_1 + M_2$ , and the respiratory flux,  $R$ , after infinite time ( $t \rightarrow \infty$ ), are given by [alternatively, equate eqn (1) to zero and solve for  $M_1$  and  $M_2$ ]:

$$\begin{aligned}M_1(\infty) &= \frac{P_n}{k_1 + k_{12}}, \quad M_2(\infty) = \frac{k_{12}}{k_1 + k_{12}} \frac{P_n}{k_2} \\ M(\infty) &= M_1(\infty) + M_2(\infty) = \frac{P_n}{k_1 + k_{12}} \left( 1 + \frac{k_{12}}{k_2} \right) \\ R(\infty) &= k_1M_1(\infty) + k_2M_2(\infty) = P_n\end{aligned}\quad (4)$$

Because  $k_1$  (respiration of the fast turnover pool)  $\gg k_{12}$  (physico-chemical reactions)  $\gg k_2$  (respiration of the stabilized pool), eqn (4) approximates to:  $M(\infty) = P_n k_{12} / k_1 k_2$ . That is, as expected, the steady-state total carbon pool can be increased by increasing the input rate,  $P_n$ , or the rate of

stabilization,  $k_{12}$ , and can be decreased by increasing the rates of microbial respiration,  $k_1$  and  $k_2$ .

Equation 4 can be used to explore the effect on total soil carbon at equilibrium of changes in rate constants and net primary production that may occur in response to warming. Table 2 presents the effect of up to four-fold increases in the rate constants, and two-fold increases in net production. Clearly, if  $P_n$ ,  $k_1$ ,  $k_2$  and  $k_{12}$  are all increased by the same factor, there is no change in  $M(\infty)$  [Table 2 (a) and (b)]. If  $P_n$  is unchanged and microbial respiration rates ( $k_1$  and  $k_2$ ) are doubled there is a large loss of carbon if the physico-chemical rate constant,  $k_{12}$ , remains unchanged [Table 2 (c)]. However, the loss of carbon is minimal if  $k_{12}$  is increased by a larger factor than  $k_1$  and  $k_2$  [e.g. four-fold compared with two-fold in Table 2 (f)]. And when  $P_n$  is increased as well as  $k_1$ ,  $k_2$  and  $k_{12}$ , the soil organic carbon pool is enlarged [Table 2 (g)].

In eqn (4) and Table 2, the effect of temperature on equilibrium soil organic carbon is evaluated numerically, by assuming that the rate constants are increased by given factors. This can be accomplished algebraically, by differentiating the organic carbon expressions in eqn (4) with respect to temperature, and denoting the temperature differentials with a prime:

$$\begin{aligned}M'_1(\infty) &= \frac{1}{k_2^2(k_1 + k_{12})^2} k_2^2 [P'_n(k_1 + k_{12}) - P_n(k'_1 + k'_{12})] \\ M'_2(\infty) &= \frac{1}{k_2^2(k_1 + k_{12})^2} \{P'_n k_{12} k_2 (k_1 + k_{12}) \\ &\quad - P_n [(k'_1 k_{12} k_2 + k'_2 k_{12} (k_1 + k_{12}) - k'_{12} k_1 k_2)]\} \\ M'(\infty) &= \frac{1}{k_2^2(k_1 + k_{12})^2} \{P'_n k_2 (k_1 + k_{12}) (k_2 + k_{12}) \\ &\quad - P_n [k'_1 k_2 (k_2 + k_{12}) + k'_2 k_{12} (k_1 + k_{12}) \\ &\quad - k'_{12} k_2 (k_1 - k_2)]\} \quad (5)\end{aligned}$$

It can be shown that if net primary production,  $P_n$ , does not respond to temperature at all, the soil carbon pool enlarges when the factor by which physico-chemical reaction rates increase is about 2.3-times the factor by which soil



microbial respiration rates increase. If, at the other extreme, net production rises in response to warming by the same factor as soil microbial respiration, then all that is required for an increase in soil carbon is that the physico-chemical reaction rates increase by a factor greater than microbial respiration rates.

In many real-world situations, the truth is likely to lie between these extremes: that is,  $P_n$  responds positively to temperature, but less than soil microbial respiration (Cannell and Thornley, 1998; Kirschbaum, 2000; White *et al.*, 2000), so that soil carbon increases if the ratio of increase in physico-chemical/microbial reactions exceeds about 1.5 (i.e. physico-chemical reactions are about 50 % more sensitive to temperature than microbial reactions).

#### A more complex model

The model in Fig. 1 may be considered too simple to demonstrate the principle being proposed. The same ideas were therefore tested in the more complex scheme shown in Fig. 3. There is no consensus about the way in which continuous soil carbon transformations can be represented in pool-based models, but Fig. 3 captures the following features which are common to many plant ecosystem soil submodels [the linear rate constants,  $k_i$  ( $d^{-1}$ ), are illustrative]:

there are three carbon pools with fast, intermediate and slow turnover rates ( $M_1$ ,  $M_2$  and  $M_3$ , respectively); net primary production ( $P_n$ ) enters the fast pool at  $0.005 \text{ kg C m}^{-2} \text{ d}^{-1}$ ;

these three pools are subject to microbial decomposition (respiration, with efflux of  $\text{CO}_2$ ) without carbon transfer between pools, with rate constants ( $\times 10^{-3} \text{ d}^{-1}$ )  $k_1 = 2.0$ ,  $k_2 = 0.2$  and  $k_3 = 0.02$ , respectively;

the three pools are also subject to microbial decomposition involving carbon transfers in both directions between all three pools; the rate constants ( $\times 10^{-3} \text{ d}^{-1}$ ) are:  $k_{12} = 1.0$ ,  $k_{21} = 0.1$ ,  $k_{13} = 0.6$ ,  $k_{31} = 0.06$ ,  $k_{23} = 0.6$  and  $k_{32} = 0.06$ , with 50 % respiration;

there is also a pool of stabilized carbon,  $M_4$ , with a very slow turnover rate ( $k_4 = 0.002 \times 10^{-3} \text{ d}^{-1}$ ) (cf. Hassink and Whitmore, 1997, who assumed no decomposition of this pool); and

there are transfers in both directions between the stabilized pool and the other three pools, which are assumed to be driven by physico-chemical processes such as adsorption and desorption and involve no efflux of  $\text{CO}_2$ ; the rate constants are chosen so that each equilibrium would be 10:1 towards the stable pool, and there is, due to the mineralization of  $M_4$ , a slow net flow of carbon to the 'stabilized' pool ( $k_{14}$ ,  $k_{24}$  and  $k_{34} = 0.002 \times 10^{-3} \text{ d}^{-1}$ ;  $k_{41}$ ,  $k_{42}$  and  $k_{43} = 0.0002 \times 10^{-3} \text{ d}^{-1}$ ).

This model was run with the above parameter values to predict the total soil carbon amount at equilibrium,  $M(\infty)$ , shown at point A in Fig. 4. To simulate a notional increase in temperature, net primary production was increased by a factor of 1.3 and all the rate constants by 1.5. As expected,

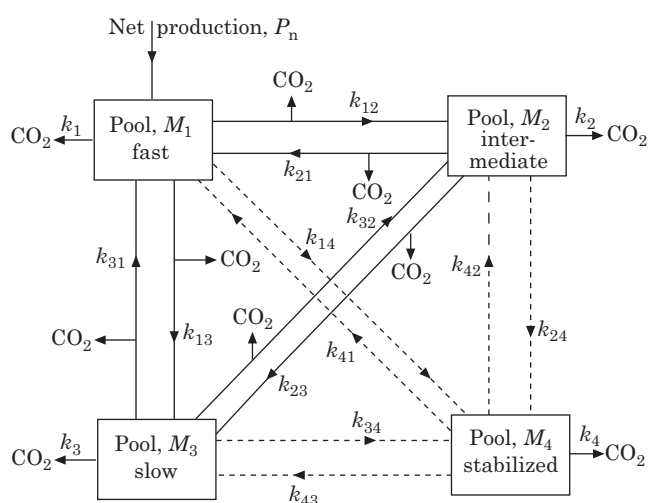


FIG. 3. A four-pool soil organic matter model, accounting for carbon flows only, and with linear kinetics throughout.  $k$  indicates a rate constant ( $d^{-1} \times 10^{-3}$ ), with standard values of:  $k_1 = 2.0$ ;  $k_{12} = 1.0$ ;  $k_{13} = 0.6$ ;  $k_{14} = 0.002$ ;  $k_2 = 0.2$ ;  $k_{21} = 0.1$ ;  $k_{23} = 0.6$ ;  $k_{24} = 0.002$ ;  $k_3 = 0.02$ ;  $k_{31} = 0.06$ ;  $k_{32} = 0.06$ ;  $k_{34} = 0.002$ ;  $k_4 = 0.002$ ;  $k_{41} = 0.0002$ ;  $k_{42} = 0.0002$ ;  $k_{43} = 0.0002$ . Net primary production  $P_n = 0.005 \text{ kg C m}^{-2} \text{ d}^{-1}$ . Microbial processes are shown with solid lines, physico-chemical processes with broken lines.

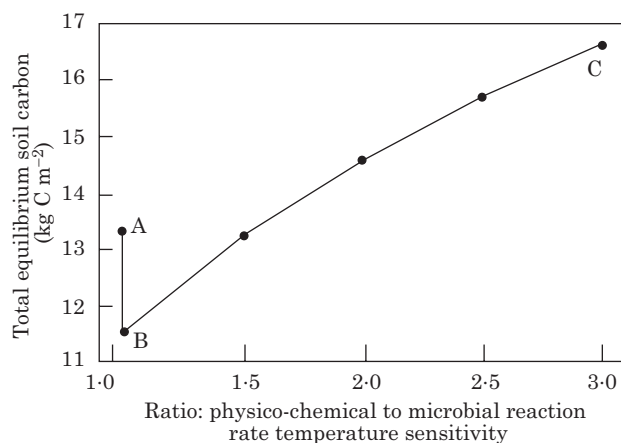


FIG. 4. Prediction of the four-pool soil carbon model in Fig. 3, showing the effect on total equilibrium soil carbon of increasing the temperature sensitivity of soil physico-chemical 'stabilization' processes relative to microbial 'decomposition' processes (respiration and mineralization). At A (at a low temperature), all rate constants have the values given in Fig. 3. At B (at a higher temperature), net production ( $P_n$ ) is increased by a factor of 1.3; microbial rate constants are increased by a factor of 1.5 ( $k_i$ ,  $i = 1$  to 4,  $k_{ij}$ ,  $i, j \leq 3$ ); and physico-chemical rate constants are also increased by a factor of 1.5 ( $k_{ij}$ ,  $i$  or  $j = 4$ ). Proceeding from B to C, the physico-chemical rate constants are further increased by the factor shown. Thus, at 2.0 on the abscissa, the physico-chemical rate constants are elevated twice as much as the microbial rate constants (by 3.0 compared with 1.5).

the model predicted a drop in total soil carbon, to point B in Fig. 4.

The physico-chemical rate constants were then increased by factors of 2.25, 3.0, 3.75 and 4.5 (above their original values, given above) so that the ratios of physico-chemical to microbial reaction rates were (dividing by 1.5) 1.5, 2.0,

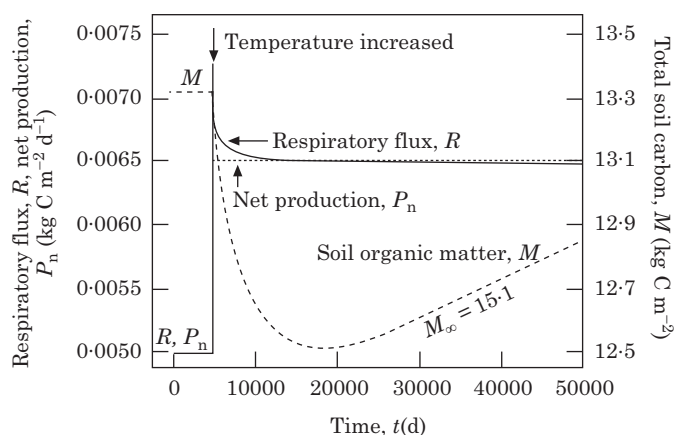


FIG. 5. Prediction of the four-pool soil carbon model in Fig. 3, showing changes in total soil carbon ( $M$ ) over time following a step increase in rate constants (simulating a notional increase in temperature). Initially, the system is in a steady state. At time  $t = 5000$  d, net production ( $P_n$ ) is increased by a factor of 1.3; microbiological rate constants are increased by a factor of 1.5 ( $k_i$ ,  $i = 1$  to 4,  $k_{ij}$ ,  $i, j \leq 3$ ); and physico-chemical rate constants are increased by a factor of 3.375 ( $k_{ij}$ ,  $i$  or  $j = 4$ ).

2.5 and 3.0, respectively. Figure 4 shows that when this ratio exceeded 1.5, the equilibrium total soil carbon was greater than it was at point A. That is, total soil carbon increased following an increase in temperature when physico-chemical reactions were accelerated over 50% more than microbial reactions. Thus, the predictions from this complex model are quantitatively very similar to those of the simple model.

Figure 5 shows the time dynamic of the system. Up to  $t = 5000$  d, the model is at equilibrium with the parameter values given above and so predicts the same equilibrium soil carbon as at point A in Fig. 4. Then, at  $t = 5000$  d, a step-wise increase in temperature is simulated by increasing net production ( $P_n$ ) by a factor of 1.3, all microbial rate constants by 1.5 and all physico-chemical rate constants by 3.375 (i.e.  $1.5^3$ ). (This is equivalent to moving from point A in Fig. 4 to a point midway between abscissa values 2.0 and 2.5 on the line.)

There is a sudden increase in respiration,  $R$ , at  $t = 5000$  d, followed by a decrease to the higher equilibrium value of  $R = P_n$ . That is, soil respiration is increased, as expected, as all microbial reactions are accelerated. However, the acceleration of physico-chemical processes means that the stabilized pool,  $M_4$ , gradually becomes populated at the expense of the three less stable carbon pools. This results in a slow accumulation of total soil organic matter, eventually leading to an equilibrium value of  $15.1 \text{ kg C m}^{-2}$ , more than its value before the temperature increase ( $13.3 \text{ kg C m}^{-2}$ ). Thus, warming accelerated soil respiration, but in the long-term, increased soil carbon.

## DISCUSSION

The purpose of this paper is to put forward an hypothesis that may help to explain why, in the long-term, soil organic carbon may not always decrease in response to warming (see Introduction) without having to assume that microbial respiration in any soil pool is insensitive to temperature. No experimental evidence is presented in support of the

hypothesis: it is presented as an idea to be tested. Such tests might involve measuring the temperature responses of pools and fluxes in soils where the biological processes have been disabled—possibly by irradiation.

It is proposed that soil physico-chemical reactions, which stabilize soil carbon and protect it from microbial respiration, may be accelerated by warming. Many reactions are involved in stabilization, some of which are likely to have positive activation energies, notably chemical adsorption (Theng, 1974; Burchill *et al.*, 1981; Schulten and Leinweber, 2000; Table 1). Those involving large molecules may have activation energies as large or larger than those of microbial respiration, which is enzyme-mediated. Reactions with large activation energies have large  $Q_{10}$  values (Thornley and Johnson, 2000, eqn 5.1) so the protection of some organic molecules could, in theory, be more sensitive to warming than soil respiration.

Both a simple analytical soil model (Fig. 2) and a more complex model (Fig. 3) demonstrate that if this hypothesis is true, warming may cause little decrease in total soil carbon in the long-term—and would cause an increase in soil carbon if physico-chemical stabilization reactions were over 50% more sensitive to temperature than microbial reactions (Table 2, Fig. 4).

The hypothesis presented does not challenge or resolve the debate on whether mineral soil carbon pools are less sensitive to temperature than litter and fast turnover pools—on which some soil respiration  $Q_{10}$  values have been based (see Introduction). Instead, it offers an alternative or additional mechanism by which soil carbon storage can remain stable or increase at warmer temperatures. If the hypothesis is true, then long-term soil carbon storage will appear to be insensitive to a rise in temperature, even if the respiration rates of all pools respond to temperature as assumed by, for instance, Lloyd and Taylor (1994) or Kirschbaum (2000).

Any observations that soil carbon storage can actually increase in response to warming cannot be explained by lowering the temperature sensitivity of microbial decomposition. This phenomenon can only be explained by

increased litter input (net primary production at equilibrium) or enhanced transfers of carbon from unprotected to stabilized, protected pools. Liski *et al.* (1999) simulated increased soil carbon at warm temperatures by making the unrealistic assumption that carbon had a fixed residence time in each pool (Ågren, 2000). Other models are unable to simulate increased carbon at warm temperatures when transfers between pools are coupled to the fraction of carbon lost by microbial respiration (Ågren and Bosatta, 1998). The hypothesis presented here offers a credible mechanism for increased soil carbon storage with increased temperature without enhanced primary production.

It should be stressed that shifts between soil carbon pools can be slow and that the hypothesis presented refers to equilibrium carbon storage, which may not be reached for decades or centuries. Figure 5 shows that soil respiration may be greatly increased with little loss of soil carbon shortly after a step-wise increase in temperature; but after some time, both respiration and soil carbon decrease and, at equilibrium, respiration (by definition) will equal net primary production and total soil carbon may have actually increased. It is clearly perilous to draw conclusions about real-world conditions from short-term warming experiments (Rustad *et al.*, 2000).

The global question of how climate change and increasing atmospheric CO<sub>2</sub> levels will alter the balance between net primary production and soil respiration can only be addressed using models. These models challenge what we know, and nowhere more so than in soil processes. Observations and experiments have prompted hypotheses such as that put forward here and by Giardina and Ryan (2000). The need now is for more experimentation at the process level.

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