Modelling the physical states, element stoichiometries, and residence times of topsoil organic matter

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Summary

Soil organic matter (SOM) is a major ecosystem component, central to soil fertility, carbon balance, and other soil functions. To advance SOM modelling, we devised a steady-state model of topsoil SOM, with explicit descriptions of physical states and properties, and used it to simulate SOM concentration, carbon:nitrogen:phosphorus (C:N:P) stoichiometry, bulk density, and radiocarbon content. The model classifies SOM by element stoichiometry (±SOM is poor in N and P, ²SOM is rich), mean residence times (1–2000 years), and physical state (free, occluded, adsorbed, hypoxic). The most stable SOM is either ²SOM preferentially adsorbed by mineral matter, or ±SOM in strongly hypoxic zones. Soil properties were simulated for random combinations of plant litter input (amount and C:N:P stoichiometry), mineral sorption capacity, propensity for hypoxia, and bulk density of non-adsorbed ±SOM. To optimize model parameters, outputs from 5000 simulations were used to construct bivariate relations among soil variables, which were compared with those found in data for 835 survey sites, covering all common land uses. The bivariate relations, and patterns of data scatter, were reproduced, and also variations in soil radiocarbon with soil type, suggesting that apparent scatter in measured data might reflect SOM diversity. The temporal acquisition by soil of 'bomb ^{14}C' could also be simulated. The steady-state model is the basis for a dynamic version, suitable for simulating changes in SOM through time. It provides insight into the possible manipulation of SOC sequestration; for example increasing litter inputs might only increase moderately-stable SOC pools, while encouraging the creation of ²SOM by adsorption to mineral matter from deeper soil could lead to long-term stabilization.

Highlights

- Models of SOM should include explicit descriptions of physical states and properties.

- Our new topsoil SOM model is constrained by C:N:P stoichiometry, $SO^{14}C$, and physical fractionation data.

- Simulated soil properties, randomly generated, account for measured trends and patterns of scatter in SOM data.

- SOM properties depend upon litter input, interactions with mineral matter, hypoxia, and bulk density.

Introduction

The organic matter of topsoils comprises plant litter and its products in various stages of decomposition and conversion, and in different physical forms, a complex dynamic system (Christensen, 2001). Understanding and quantification of this system, its relationships to wider ecosystem conditions, and responses to environmental change, are necessary for management and prediction for agriculture, carbon storage and ecosystem conservation. An important part of the process is the incorporation of empirical research results and new conceptual insights into models. In turn, model outputs can provide further insights, suggest new experiments, and simulate changes at larger spatial and longer temporal scales.

The most well-established, widely-used and influential quantitative models of soil organic matter (SOM), Roth-C (Jenkinson & Rayner, 1977) and Century (Parton *et al.*, 1988), are based on organic matter pools and their first-order turnover rates, and were designed for the simulation of mineral topsoils, primarily agricultural. As more research has been conducted, and new theories developed, the absence of specific mechanisms in these models has become increasingly apparent. In a recent review, Campbell & Paustian (2015) considered how analytical and conceptual advances could be used to improve model realism. In terms of the soil processes that are responsible for storing and stabilizing SOM, they drew attention to protection against microbial attack by either occlusion in microaggregates or adsorption to mineral surfaces (Six *et al.*, 2002; von Lützow *et al.*, 2006; Kögel-Knabner *et al.*, 2008). They noted the trend towards disregarding 'humification' reactions supposed to render SOM chemically recalcitrant (Schmidt *et al.*, 2011; Dungait *et al.*, 2012; Lehmann & Kleber, 2015). However, they questioned whether the explicit modelling of microbes, which

is strongly favoured by some authors (e.g. Cotrufo *et al.*, 2013; Wieder *et al.*, 2015), is appropriate for longer-term models, primarily because of the lack of input data. Although parameterized modelling of aggregate formation was reported by Segoli et al. (2013) for use in incubation studies, and relatively complicated parameterized models with explicit simulation of adsorption alone (Hassink & Whitmore, 1997; Michalzik *et al.*, 2003; Ahrens *et al*., 2015), or adsorption and aggregate formation (Mazzoleni *et al*. 2012), have been developed, suitable representations of these processes in a new generation of widely-applicable models are awaited. Some recent thinking about SOM is included in a new conceptual model put forward by Abramoff *et al.* (2018), which has five, measurable, soil carbon (C) pools (particulate, low molecular weight, aggregated, mineral-associated, and microbial), but this model has yet to be quantitatively implemented.

The foregoing summary refers largely to aerobic mineral soils, with C concentrations typically less than 10%. In less aerobic soils, an additional stabilization mechanism operates, exclusion of the oxygen required for mineralization (Schimel *et al.*, 1994; Keiluweit *et al.*, 2017). The occurrence of hypoxia because of excess rainfall, or poor drainage, or both, is implicit in models of peat formation (Frolking *et al.*, 2001; Heinemeyer *et al.*, 2010), and in the ECOSSE model, developed by Smith *et al.* (2010) from RothC and DAISY (Bradbury *et al.*, 1993). A complete approach to SOM modelling requires both aerobic (or mineral) and hypoxic (or organic) soil properties to be simulated.

The focus in SOM models, conceptual and quantitative, is very much on C. Thus, the reviews by Campbell & Paustian (2015), Stockman *et al.* (2013), Luo *et al.* (2016) and the new model of Abramoff *et al.* (2018) hardly mention nitrogen (N) and phosphorus (P), and

although both N and P are included in Century, ECOSSE and N14CP (Davies *et al.*, 2016), they are forced to follow C. Consequently, the important role of N in SOM stability (Knicker, 2011) is disregarded, and the same might apply also to P. That N and P may provide valuable modelling constraints is shown by the recently demonstrated systematic relations involving C, N, P and sulphur (S) in SOM (Tipping *et al.*, 2016). An important finding was that N:C, P:C and S:C ratios are largest at small C concentrations, where soil mineral matter is most dominant, leading to the conclusion that mineral matter selectively adsorbs organic molecules that on average are rich in N, P and S, in accord with ideas advanced by Kleber *et al.* (2007) and Knicker (2011). Density fractionation results also point to large N:C and P:C ratios in mineral associated OM (Schrumpf *et al.*, 2013; Adams *et al.*, 2017).

To address the issues described above, we developed a new steady-state model in which stoichiometrically-differentiated topsoil SOM exists in different physical states: free (unprotected), occluded in aggregates, competitively adsorbed, and in hypoxic zones. We carried out parameterization and testing using field data from surveys of 835 British soils at sites with land uses covering arable agriculture, intensive pasture, upland grazing, woodland and peatland, and including almost 100 measurements of bulk soil radiocarbon (^{14}C). The main aim was to evaluate how well the model could account simultaneously for C, N and P pools and concentrations, N:C and P:C ratios, and ^{14}C values, with physically realistic processes, parameters and controlling variables such as litter input and mineral matter properties. We used the results to consider how a corresponding dynamic model could be developed, and the implications of the findings for promoting soil C storage.

Model description

We use SOC, SON and SOP to refer to specific elements, and SOM more generally. Pools are expressed as $gC\ m^{-2}$, $gN\ m^{-2}$ and $gP\ m^{-2}$, concentrations of SOC, SON and SOP are in % ($g\ 100g^{-1}$), fluxes in $g\ m^{-2}\ a^{-1}$. For soils with an O horizon, we include it as part of the topsoil, rather than considering just the mineral soil, as is sometimes done (e.g. Crow *et al.*, 2007; Schrumpf *et al* 2013).

The postulated pools and fluxes of SOC are shown in Figure 1, for mineral and organic soils, which are treated separately here for clarity. The mineral soil model is a simplification of the conceptual model of Six *et al.* (2002), including stabilization by occlusion (i.e. within microaggregates), and by adsorption, but disregarding the concept of stabilization through chemical recalcitrance. In the organic soil model, SOM is stabilized both by adsorption and by existing in weakly- or strongly-hypoxic zones, SOM_{hypox1} and SOM_{hypox2}, respectively, but not by occlusion. There are two stoichiometric types of SOM and adsorbable dissolved organic matter (DOM); the $\pm$ form is relatively poor in N and P, the ^{2} form relatively rich. The $\pm$SOM is present in SOM_{free} (unchanged plant litter), in SOM_{occ}, SOM_{hypox1} and SOM_{hypox2}, and in adsorbed states, whereas ^{2}SOM exists only in mineral-adsorbed forms. Having the same stoichiometry for $\pm$SOM and $\pm$DOM is a simplification used for the present analysis. Apart from the fluxes of adsorbable DOC, losses of C from the soil pools are considered to be losses from the system (indicated by horizontal arrows in Figure 1), as either CO_2-C or DOC, i.e. there is no recycling of desorbed DOC. Excess (not adsorbed) DOC is also lost from the system.

As well as being quantified in terms of mass (gC m^{-2} and g mineral matter (MM) m^{-2}), the soil constituents are quantified by volume (cm^3 m^{-2}), related to the mass pools by the bulk densities (g cm^{-3}) of the individual components. Occluded and adsorbed SOM are assigned the same bulk density ($\rho_{occ,ads}$); SOM_{free}, SOM_{hypox1} and SOM_{hypox2} have a separate value ($\rho_{free,hypox}$). The value of ρ_{MM} is assumed to be the same for all mineral matter.

Model equations (see Supporting Information) describe the following features:

(1) Outputs of SOC from the model pools are governed by rate constants for first-order loss, e.g. k_{free} (Table 1). For four of the model pools (Figure 1), outputs of OC are partitioned into two, three or four different forms; in these cases the sum of the fluxes equals the total first-order loss flux from the parent pool.

(2) In mineral soils, the fraction of the $\pm SOC_{free}$ loss flux that transforms to $\pm SOC_{occ}$ depends upon the clay content of the soil (cf. Six *et al*., 2002). The model does not use mineral textural properties explicitly; as a proxy for clay content we use the product of the total SOC adsorption capacity, σ_{MM}, and the MM pool. This assumes that the greater the amount of clay in the soil, the greater will be its adsorption capacity.

(3) Organic soils have varying amounts of hypoxically-protected $\pm SOM$ that decomposes slowly because of restricted oxygen supply. Type 1 hypoxia is less intense than type 2. The transfers of $\pm SOM_{free}$ to $\pm SOM_{hypox1}$ and $\pm SOM_{hypox2}$ depend on the volume of soil that can potentially become hypoxic ($V_{hypox,pot}$). A maximum volume, $V_{SOM\_hypox1,max}$, that can be occupied by $\pm SOM_{hypox1}$ is defined, and if this equals or exceeds $V_{hypox,pot}$ then only $\pm SOM_{hypox1}$ can exist. Otherwise, any volume remaining, i.e. ($V_{hypox,pot} - V_{SOM\_hypox1,max}$), is occupied by $\pm SOM_{hypox2}$, subject to the availability of $\pm SOM_{free}$.

(4) A fraction of the loss from SOM_{free}, SOM_{occ}, SOM_{hypox1}, and SOM_{hypox2} comprises ±DOM and ² DOM. Both DOM forms can adsorb to MM, depending upon the size of the MM pool and its complement of sorption sites. The sorption sites comprise two classes, strong and weak, to account in a simple way for surface heterogeneity. A key assumption of the model is that ² DOM is preferred over ±DOM by the strong adsorption sites. If the sorption sites are insufficient to take up all the DOM, there is an excess flux of ±DOM and/or ² DOM (Figure 1).

(5) For comparison with density fractionation results for mineral soils, the SOM_{free} pool is equated with the free light fraction, fLF, and the aggregate-protected pool with occluded LF, oLF (see e.g. Schrumpf *et al*., 2013). Thus the amount and composition of the total LF are obtained from the sum of ±SOM_{free} and ±SOM_{occ}. The heavy fraction (HF) SOM comprises ±SOM_{wkads}, ² SOM_{wkads}, ±SOM_{strads} and ² SOM_{strads}.

(6) Radiocarbon contents of the different SOM pools in a given year are obtained from their loss rate constants, the atmospheric ^{14}C signal, and a steady-state turnover model (Mills *et al.*, 2014). Variations in ^{14}C reflect radioactive decay, which depends on the turnover of longer-lived pools, and the acquisition by photosynthesis and litter production of 'bomb carbon' from atmospheric thermonuclear weapons testing during the mid twentieth century. For simplicity, we assume that all plant litter is produced during the same year as photosynthetic uptake, disregarding any longer-term storage of ^{14}C in plant tissues, e.g. roots and tree twigs. Except during the period around the atmospheric 'bomb C' peak (1960-1975), for which no soils data were used in this work, we estimate that such storage would alter simulated topsoil ^{14}C values by less than ±2.0 percent modern absolute (pMC), more

typically by less than ± 1.0 pMC. Such discrepancies can be considered negligible compared to the ranges of values of $SO^{14}C$ in our data. Account is taken of the passage of some SOM though more than one pool (Bruun *et al.*, 2004), which means that the DOM forms released from SOM_{free}, SOM_{occ}, SOM_{hypox1}, and SOM_{hypox2} differ in their ^{14}C contents when adsorbed by MM. The ^{14}C contents of bulk soil, LF and HF are obtained from the proportions of the contributing pools.

Methods

Soils data

Soil survey data for Great Britain were taken from Emmett *et al.* (2010) and Toberman *et al.* (2016). Measured topsoil (15 cm depth) variables used for modelling comprised %OC, % total N, %OP and bulk density. Organic N was approximated as total measured N, which is on average 95% organic N (Schulten & Schnitzer, 1998). Additional variables calculated from the measured data were C, N and P pools and N:C and P:C ratios. In all, 835 field sites were sampled, although only for the 65 sites sampled by Toberman *et al.* (2016) did the data include %OP. We used density fractionation data for British soils from Adams *et al.* (2017).

Radiocarbon data were taken from results for samples collected in 2007 (Mills *et al.,* 2014) and 2013 (Toberman *et al.,* 2016), and assumed to apply to the intermediate year, 2010. An approximate average value of 110 pMC for topsoil ^{14}C in 1980 was taken from the global (mostly North American) compilation of Harrison (1996); the need for temporally-separated ^{14}C values arises because the model ought to produce an upturn and subsequent decline in soil ^{14}C in response to the input of 'bomb' radiocarbon in the mid twentieth century (Harrison, 1996; Jenkinson *et al.*, 1992; Tipping *et al.*, 2010). The 65 samples from Toberman *et al.* (2016) were tested for the presence of charcoal and coal, negligible amounts being found. The Mills *et al.* (2014) samples had not been checked. Data for four samples from Mills *et al.* (2014) and two from Toberman *et al.* (2016) were omitted from the analysis; these all had [14]C < 90 pMC and were judged to be atypical.

Additional data were taken from the WISE database (Batjes, 2009) and from Tomar (2000) to test model-predicted relations involving C, N, P and bulk density. Radiocarbon and related soil data for testing predicted temporal variations in ^{14}C were taken from Torn *et al.* (2002) for a natural grassland site in Russia, Baisden & Parfitt (2007) and the New Zealand Soils Bureau (1968) for a pasture in New Zealand, Tipping *et al.* (2010) for a UK broadleaf forest, and Fröberg *et al.* (2011) for Swedish coniferous forests.

Parameter and input values

Parameters are single-value fixed quantities for all soils (Table 1), while input values (Table 2) are either true variables (e.g. litter input rate) or loss rate constants for passive pools that vary among soils. These values are sampled from even distributions within defined ranges, as inputs to the model. Some of the parameter values, and some ranges of input values, could be set *a priori*, others were fitted to the data.

Loss rate constant values were based on previous work such as the Century model (Parton *et al.*, 1988), Mills *et al.* (2014), and N14CP (Davies *et al.*, 2016), with fast (or active), slow and passive pools having mean residence times (MRT) of *c.* 1, 20 and 1000 years respectively (k values of 1, 0.05 and 0.001 year^{-1}). The slow pool is needed to simulate the effect on soil ^{14}C of the input of 'bomb carbon' since the mid twentieth century, as mentioned above. In mineral soils the slow pool comprises $\pm SOM_{wkads}$, $^{2}SOM_{wkads}$ and $\pm SOM_{strads}$, whereas in organic soils it comprises these three pools together with $\pm SOM_{hypox1}$. The MRT of SOM_{occ} is about 100 years (Crow *et al.*, 2007; Meyer *et al.*, 2012), therefore k_{occ} = 0.01 year^{-1}. The passive pool is $^{2}SOM_{strads}$ in mineral soils, $^{2}SOM_{strads}$ and $\pm SOM_{hypox2}$ in organic soils. After initial trials, it was decided to treat $k_{2,strads}$ and k_{hypox2} as input variables,

with values centred on 0.001 year^{-1}, to simulate scatter in the ^{14}C data. The value of $k_{\text{free,occ}}$ was set to 1×10^{-6} m^2 gC^{-1}, which, when combined with the chosen ranges of litter input and adsorption site densities (see below) ensured that pools of $\pm$SOM$_{\text{occ}}$ were in the range zero to 1000 gC m^{-2}, in accordance with observations of occluded LF (Crow *et al.*, 2007; Meyer *et al.*, 2012; Schrumpf *et al.*, 2013).

The soil volume was set to 1.5×10^5 cm^3 m^{-2}, corresponding to a stone-free soil depth of 15 cm, to coincide with the sampling depth (see above). The fraction of organic matter that is C was set to 0.55 (Emmett *et al.*, 2010). The maximum fraction of the soil volume that can be $\pm$SOM$_{\text{hypox1}}$ was set to one-third, bearing in mind the need to represent conifer and other podzols with O horizons of *c.* 5-cm thickness. We set the hypoxic volume fraction for organic soils to a range of 0.2–0.995.

The bulk densities of $\pm$SOM$_{\text{occ}}$ and all adsorbed forms of SOM were assumed to be the same; $\rho_{\text{occ,ads}}$ was optimised in the fitting process, as was ρ_{MM}. The bulk density of free and hypoxic SOM, $\rho_{\text{free,hypox}}$, was treated as an input variable, with a range of 0.05 to 0.15 g cm^{-3}, based on measured data for the most organic-rich soils ($\sim$ 50 %C). The adsorption capacity of MM, σ_{MM}, was assumed to range from 0.01 to 0.2 gC gMM^{-1}, based on data for soil heavy fractions (Swanston *et al.*, 2005; Crow *et al.*, 2007; Schrumpf *et al.*, 2013; Adams *et al.*, 2017) and size-fractionated soils (Makarov *et al.*, 2004; Moni *et al.*, 2012).

The model includes three fractional quantities, namely f_2 (fraction of DOM that is ^{2} DOM), f_{str} (fraction of adsorption sites that are strong), and $f_{\text{SOM,DOM}}$ (fractional loss to DOM from $\pm$SOM pools). Each was treated as a parameter and optimized by comparison of model outputs with measured data.

The element stoichiometry of ±SOM was set to three-fold ranges of 0.0165 to 0.0495 for N:C and 0.0006 to 0.0018 for P:C, based on data for the soil light fraction (Schrumpf *et al.*, 2013; Adams *et al.*, 2017), temperate litter composition (Trofymow *et al.*, 1995), and from end-member modelling (Tipping *et al.*, 2016). Three-fold ranges for the N:C and P:C ratios of ^{2} SOM were optimised.

We used a range of 50 to 800 gC m^{-2} year^{-1} for litter inputs based on vegetation productivity data for UK grasslands, shrublands and woodlands (Table S1, Supporting Information), adjusted for below-ground production, and allowing that OM supplies to arable soils might be small because of harvesting.

Calculation procedure

The field data provide a large sample, but we lack site-specific information for model inputs. Therefore we compared the properties (trends, scatter) of the measured data with simulated values derived from random combinations of the model input variables (Table 2). A value for each input variable was chosen randomly from the fixed ranges or those ranges being optimized, for 5000 different examples. We chose to simulate 3333 mineral soils and 1667 organic soils, because of the greater logarithmic range of %C in the former. These numbers of simulations were sufficient to produce essentially unvarying results for different sets of random choices.

Firstly, the size of the SOM$_{free}$ pool was calculated from the litter input rate and the loss rate constant k_{free}. For a mineral soil, the remaining soil volume was then partitioned among the remaining SOM pools by iteratively adjusting the size of the MM pool while computing the sizes of the occluded and adsorbed pools. For an organic soil, the SOM$_{hypox1}$

and SOM$_{hypox2}$ pools were computed from the chosen available hypoxic volume, then the MM pool was calculated iteratively, to obtain the value that corresponded to the filled total soil volume. Calculations were done with Microsoft Excel. A version of the model capable of simulating a single soil is included in Supporting Information.

Fitting procedure

Fitting was done by comparing derived quantities characterizing measured data with the equivalent quantities for the simulated results. In 10 cases, this meant comparing slopes and intercepts of linear bivariate relations (Table 3(a)), while in five cases average or percentile values were used (Table 3(b)). Because both x- and y-axis values are subject to error, bivariate constants were derived using reduced major axis regression.

The objective function to be minimized was the sum of weighted squared differences between the quantities (slopes, intercepts, average values) derived from the measured and simulated data (standardized by dividing each difference by the quantity derived from measurements), a total of 25 different values. In choosing the weighting factors, we judged it important to obtain good agreements for the slopes of log_{10} %N against log_{10} %C, log_{10} %P against log_{10} %C, BD against log_{10} %C, and the individual averages of ^{14}C in 1980 and 2010 (see Table S2, Supporting Information). We used the Solver function in Microsoft Excel to optimise the five adjustable parameter values (Table 1), and the two stoichiometric ranges for ^{2} SOM (Table 2). We tested the sensitivity of the model by systematically fixing individual values of parameters or input variables, and then re-fitting.

As described above, the fitting procedure relies on reproducing trends in the data, rather than measured quantities for individual soils. Therefore multivariable matching (i.e.

matching of all available quantities for each soil) was done to check that each property of a single real soil could be reproduced in one or more single simulated soils. The simulated soil most closely matching a given real soil was taken to be the one with the smallest sum of squared residuals between the full suite of measured and simulated variables (BD, %C, N:C ratio, P pool, ^{14}C content etc). A few large residuals might contribute to the smallest sum of squared residuals, producing a skewed match, therefore we averaged simulated data for the three simulated soils that best-matched each real soil. A large weighting was given to residuals of ^{14}C values, otherwise ^{14}C values did not match well.

Correlation coefficients (r) and probabilities (P) associated with reduced major axis regression were used to compare observed and simulated bivariate relations between soil variables, and in the evaluation of multivariable matching. They were calculated with the lmodel2 package (version 1.7-3) in R (R Core Team, 2013).

Results

Optimization of the five adjustable parameters and the two adjustable ² SOM stoichiometry ranges (Tables 1 and 2) yielded the slopes, intercepts and mean quantities shown in Table 3. The agreements between the quantities derived from measured and simulated data are generally quite close, within 10% for 15 of the 25 quantities and within a factor of two for all but two quantities. The correlation values, r, agree reasonably. The data patterns for the measured and simulated data are generally very similar (Figure 2). The simulated mineral soils have SOC contents ranging from 0.4 to 14.4%, with a median of 4.5% and a mean of 5.0%, and the corresponding values for organic soils are 0.9% – 53.5%, 13.7% and 17.2%. Thus, there is appreciable overlap of the two soil types with respect to SOC. Note that the model permits the existence of organic soils with small %C values, which form if there are small hypoxic zones and low litter input rates; routine bulk analyses would not identify such soils as organic.

The two bulk density parameters are physically realistic; ρ_{MM} is approximately the same as measured whole soil values at small %C, while $\rho_{occ,ads}$ is somewhat greater than the bulk density of highly organic soil, indicating that adsorbed or occluded SOM is slightly denser than SOM not associated with MM. The average values (within the assumed threefold ranges) of N:C and P:C for ±SOM and ² SOM are defined approximately by the ranges of the measured values (Figures 2(j,k,l)), and so are also physically realistic. Three parameters, f_2, f_{str} and $f_{SOM,DOM}$, are model constructs constrained to fall between zero and unity. Their values could be varied only within modest ranges, $c.$ ±30%, without changing the value of the objective function by more than 5%, and so they are quite well-defined. The value of

$f_{SOM,DOM}$ means that 37% of the C lost from ±SOM in its decomposition is in DOM, the remainder being primarily CO_2-C, and the value of f_2 means that 6.3% of the DOC is in ^{2} DOM, which represents a small but important flux (see below). The value of f_{str} means that 25% of the adsorption sites of MM are in the strong category; this can be considered only a rough division for modelling purposes, since the adsorbent-adsorbate systems must be quite complex and variable among soils.

Figure 2 compares model outputs with observations, and shows that the measured data are represented well by the simulations. In particular, there is agreement for the variations in $\log_{10}$ %N and $\log_{10}$ %P with $\log_{10}$ %C (panels a and b), and of N:C and P:C with $\log_{10}$ %C (panels j and k), accounting for the strong tendency of the N:C and P:C ratios to decrease with %C. The patterns of scatter in the observations and simulations are similar, and arise in the simulations from variations in the input variables. The effects of the different input variables can be seen in Figure S1 (Supporting Information).

There were also relations involving BD, N, P and C in topsoil global data, from the WISE database and Tomar (2000), and these largely overlap our simulations (Figure S2, Supporting Information), although the agreement is relatively poor for BD, which is considerably more variable in the WISE data.

Radiocarbon

Measured radiocarbon values for 2007–2013 increase weakly but significantly with %C ($R^2 = 0.14$, $P < 0.001$) and the SOC pool ($R^2 = 0.04$, $P < 0.05$) and decrease weakly but significantly with N:C ($R^2 = 0.07$, $P < 0.01$), and the simulations show the same trends (Figure 2). These trends were not used for fitting, but it was evident from inspection of the

plots that to generate the necessary scatter in ^{14}C, ranges had to be assigned to the values of $k_{2,strads}$ and k_{hypox2} (Table 2); this can be appreciated by comparing Figures 2 and S1(d) (Supporting Information). For ^{14}C variation with N:C, a smaller contribution to the scatter arises from variation in the N:C ratios of ±SOM and ²SOM.

Multivariable matching (see Methods) of measured data for four sites or regions for which temporal ^{14}C data were available was used to test the model's ability to reproduce temporal variation in ^{14}C following atmospheric enrichment in ^{14}C by atmospheric weapons testing. Reasonable agreement was obtained between available measured and simulated values of element pools, concentrations, and BD (Table S3, Supporting Information). The simulated variations in ^{14}C over time are compared with observations in Figure 3. Note that in this exercise we were attempting to match a number of soil variables at the same time, and therefore were unable to adjust k or MRT values to match the ^{14}C values precisely, as has been done in previous radiocarbon studies (e.g. Harrison, 1996; Tipping *et al.*, 2010). The exercise confirms that the model predicts rises and falls in ^{14}C of the right timing and magnitude.

Pools of C, N and P

Simulation outputs for average soils with different %C (Figure 4) show dominance of the adsorbed pools at small %C, and the increasing importance of the hypoxic forms as %C increases. Whereas for C the total pool increases with %C, only falling slightly at the largest %C, maxima for N and P are seen at around 10%C, reflecting the importance of adsorption for retaining these elements.

This is further demonstrated by results for the average simulated mineral soil (4.7% C), in which 85% of the SOC is in the adsorbed pools, but 93% of the SON, and 99% of the SOP, a trend which agrees with the density fractionation results of Adams *et al.* (2017). Moreover, while 35% of SOC is present as ^{2}SOC$_{strads}$, the values for SON and SOP are 64% and 88% respectively. Since the ^{2}SOC$_{strads}$ pool has an MRT of 667–2000 years, it follows that most mineral topsoil organic N and P are in slow turnover pools, playing minor roles in nutrient cycling.

The same conclusions apply qualitatively to the average simulated organic soil (16.6% C), with 34% of the SOC, 54% of the SON, and 84% of the SOP in adsorbed pools. The additional SOM in the hypoxic pools means that the importance of the adsorbed forms is less. In the most organic-rich soils (> 50%C), the adsorbed N and P pools are nearly negligible (Figure 4).

Simulated occupancy of adsorption sites

The high affinity of the strong adsorption sites for ^{2}DOM, and to a lesser extent their affinity for ±DOM, means that these sites are saturated in the majority (92.5%) of the simulated soils, and the average degree of saturation is 97%. The corresponding figures for the weak adsorption sites are 27% and 49%.

Fluxes of C

The main fluxes of C through the average mineral soil (Figure 5) are from SOC$_{free}$ to CO_2 and from SOC$_{free}$ to the adsorbed ±SOC forms, as DOC. Much smaller fluxes maintain the SOC$_{occ}$ and ^{2}SOC pools. These differences reflect the longer MRTs of the SOC$_{occ}$ and ^{2}SOC$_{strads}$

pools, and the relatively small size of the ^{2}SOC$_{wkads}$ pool. In the average organic soil, there is an additional large flux from SOC$_{free}$ to SOC$_{hypox1}$, and an additional small flux maintains the SOC$_{hypox2}$ pool. The small flux needed to maintain the ^{2}SOM$_{strads}$ pool explains the small value of f_2, the fraction of DOM in the ^{2} form (Table 1).

The average excess fluxes of unadsorbed DOC in both soils (Figure 5) are comparable to, but generally larger than, measured values of DOC drainage fluxes in the field (Buckingham *et al.*, 2008; Kindler *et al.*, 2011). Over the 5000 simulated soils, there is a wide range of values, 0–310 gC m^{-2} year^{-1}, which exceeds the measured range appreciably. This implies that not all the excess DOC is leached from the soil, which means that there can be additional mineralization of DOM, not simulated in the present version of the model.

Soil volume

Bulk density model parameters estimated by fitting (Table 1) are similar to the values of 0.223 and 1.27 g cm^{-3} for SOM and MM respectively found by Adams (1973) for Welsh podzols, and to those reported by Federer *et al.* (1993) for New England forest soils, which were 0.11 g cm^{-3} for SOM and 1.45–2.19 g cm^{-3} for MM, depending upon texture. Here we distinguish free SOM, assigned a range of 0.05 to 0.15 g cm^{-3}, from the denser SOM in aggregates or adsorbed to MM.

The low bulk density and large porosity of SOM mean that soil space is dominated by SOM except in soils with small %C (Figure 4). At about 5% C, SOM accounts for 50% of the soil volume. Because we have a fixed topsoil volume in the model, competition between SOM and MM for space constrains the build up of mineral-associated SOM.

Sensitivity to key input variables

The main factors affecting the composition of mineral soils are litter input and adsorption capacity. When all parameter and input values were held constant, and only litter input was varied (Figures 6(a) and 6(b)), the SOC pool increased with litter input, but the nature of the SOC changed. At small litter inputs, SOC accumulated at the strong adsorption sites, primarily as ² SOC_{strads}. With increasing litter input, more SOC accumulated, but only in the weaker-sorbing forms, ±SOC_{wkads}, ±SOC_{strads} and ² SOC_{wkads}; the pool of ² SOC_{strads} actually decreased because the pool of MM decreased, to make space for the additional SOM. Thus, mineral soils with relatively large SOC pools are dominated by relatively unstable SOM. In soils receiving the same litter input (Figure 6(c)) ² SOC, chiefly in the ² SOC_{strads} form, increased with adsorption capacity, becoming dominant at the highest adsorption capacity. There was also an increase in SOC_{occ}, because the model assumes that the larger is the clay content of MM (proportional to adsorption capacity), the greater is the tendency for aggregates to form.

The compositions of organic soils also depended on litter inputs and MM adsorption capacity, and on their potential to develop hypoxic zones. If the potential hypoxic volume was relatively small, then the model allowed only SOC_{hypox1} to form, as in Figure 5(d), and when this space was filled, additional litter input went to the adsorbed ±SOC pools. When the potential hypoxic volume was larger, SOC_{hypox2} could also exist, but this involved only small input fluxes, and so the total SOC pool was maximal at relatively small litter input rates (Figure 6(e)). In such soils, most of the SOC is in the hypoxic forms. This results in a situation where the total C pool in the 0–15 cm layer cannot be increased by the addition of

litter above *c.* 200 gC m^{-2} year^{-1}. Under such circumstances peat might accumulate, by the effective burial of excess SOC.

Explanations of how the model produces the trends and scatter in the simulated outputs plotted in Figure 2 are presented in Table 4.

Matching soils / multivariable survey

We tested whether simulated soils could be found that gave multivariable matches to observed soils (see Methods), using the Toberman *et al.* (2016) data set, for a total of 66 soil samples, finding the best values of %C, %N, %P, C pool, N pool, P pool, ^{14}C, and BD. The simulated %C, %N and %P values tended to be smaller than the observed, especially N which had an average simulated-to-observed ratio of 0.83, the worst agreement of all. The simulated C, N and P pools tended to be greater than the observed values. Perfect matching would give all ratios of calculated to measured variables a value of 1.00. The overall average for all the variables (66 × 8 = 528 cases) was 1.03 with a standard deviation of 0.23, therefore 95% of the ratios were within the range 0.58 to 1.48, which can be considered successful matching.

The matching involved averaging the three best matches in each case. For some soils, all three matches were simulated as mineral, for others all three as organic, but in about one-third of cases the simulated soils were mixtures of mineral and organic, even for some arable soils. The matching indicated that nearly all acid soils were organic, and most non-agricultural, i.e. semi-natural, soils were organic (Figure S3, Supporting Information).

After dividing the field sites into four categories, arable (*n*=16), heath–rough grassland (18), improved pasture (20), and woodland (12), the averaged litter inputs (gC m^{-2}

year^{-1}) were calculated to be arable 107, improved pasture 262, woodland 488, and heath–rough grassland 498. These differed significantly from one another (*t*-test, $P < 0.001$) except for heath–rough grassland and woodland, and they are in fair agreement with published estimates for the different land uses (Table S1).

A second assessment of the results compared modelled adsorption capacities, σ_{MM} (gC gMM^{-1}), with clay and clay+silt contents of the soils (g gMM^{-1}), for which measured data were available in 56 cases. Because σ_{MM} would be expected to depend on the content of finely-divided, large surface area, MM, its value should increase with the clay or clay+silt content. There were significant relations for both clay and clay+silt, stronger for the latter (Figure 7). To comply with the model's expectations, if clay and silt account for the adsorption capacity (maximum 0.2 gC gMM^{-1}), the slope of σ_{MM} plotted against clay+silt content should be 0.2 gC g^{-1}, and the intercept should be zero. These criteria are nearly met by the results, albeit with considerable scatter (Figure 7).

Discussion

That the simulated soils possess the combined properties of real soils was demonstrated by the results of the multivariable matching exercises for (i) temporal variation in radiocarbon and (ii) the properties of the 66-soil data set, including sensible estimates of litter inputs, and the statistically significant relation between deduced adsorption capacity and measured clay+silt contents (Figure 7). Comparison of model simulations with independent data from other biomes (Figure S2) suggests that the modelling approach applies globally. The successful simulation of a range of data trends and scatter (Figure 2) suggests that SOM is a mixture, and that apparently simple relations, notably between litter input and the total SOC pool (Figure 6), might arise from complex variation in the responses of contributing SOC pools. Therefore apparent scatter in measured data is explicable in terms of SOM diversity.

Adsorbed SOM

A key model assumption is that selective adsorption, and consequently high stabilization, of ² SOM (large N:C and P:C) is responsible for the relations among N, P and C (Figure 2). The strong adsorption sites of MM select ² DOM molecules, so that when steady state is reached a persistent SOM pool, ² SOM$_{strads}$, exists. The molecules comprising ² SOM accumulate by a common process, adsorption, not because they have a common source or chemistry.

Most mineral soil N is calculated to be in ² SOM, and according to Knicker (2011), most SON is in peptides, the N:C ratio of which is about 0.3 g g^{-1}. Because the average N:C of ² SOM is about 0.12 (Table 2), not all the ² SOM molecules can contain N. This is consistent with the results of Nelson & Baldock (2005) for the clay-sized particles of an Australian Mollisol, which had an N:C of 0.13 g g^{-1}, and contained about 40% protein. Much

soil organic P is in inositol phosphates (Dalal, 1977; Turner *et al.*, 2002), which can adsorb strongly to oxide surfaces, in particular phytic acid (Anderson *et al.* 1974; Celi & Barberis, 2006). The P:C ratio of inositol monophosphate is 0.43 g g^{-1}, while that of phytic acid is 2.6 g g^{-1}, both of which greatly exceed the average ^{2} SOM P:C of 0.030 (Table 2), which means that only some of the ^{2} SOM molecules contain P. This is consistent with the idea that ^{2} SOM comprises molecules selected by adsorption; only on average are they rich in N or P, some contain neither element. Because peptides do not contain P and inositol phosphates do not contain N, the N and P must often be in separate molecules, but co-occurrence in nucleic acids is possible (Levy-Booth *et al.*, 2007). Although ^{2} SOM is rich in N and P, this does not mean that all N- and P-rich molecules need be adsorbed.

The model assumes that adsorbed SOM comes from DOM, mostly released from SOM_{free} but also from SOM_{occ} and SOM_{hypox1} (Figures 1 and 5). The DOM could comprise products derived directly from plant litter and also products of microbial processing. Given that the N:C ratio of total SOM arises from selection by adsorption, there is no obvious reason, according to the model, for its component molecules to come preferentially from plant litter or microbes. This idea accords with Kramer *et al.* (2017) who concluded, from sequential density fractionation and ^{15}N data, that mineral association exerts a greater control on the variation of SOM C:N ratios with soil depth, than does *in situ* organic matter decay.

To simulate adsorbed SOM pools, we assumed that adsorption strength is inversely related to the loss rate constants $k_{\pm,wkads}$, $k_{2,wkads}$, $k_{\pm,strads}$ and $k_{2,strads}$, and heterogeneity in mineral surfaces was approximated by assuming weak and strong adsorption sites. We incorporated simple competition, such that the greater was the combination of adsorption

strength and DOM flux the greater wass the extent of adsorption (Equations S19–S28, Supporting Information). However, we recognise that adsorption of DOM by MM in soil is a much more complex process, with much greater heterogeneity in both DOM and mineral surfaces than we allow (Kaiser & Guggenberger, 2003; Kleber *et al.*, 2015). It depends upon clay mineralogy, solution chemistry (Weng *et al.*, 2006; Rasmussen et al., 2018) and possibly involves aggregation of adsorbed material (Kaiser & Guggenberger, 2003; Piccolo, 2016), even to the extent of systematic multilayer formation (Kleber *et al.*, 2007). Such complexity might partially explain why, although there is a significant relation, there is also appreciable scatter in the plot of σ_{MM} against measured clay+silt content of soil (Figure 7).

Occluded SOM

This relatively small pool comprises SOM isolated by its incorporation in microaggregates. It differs from total microaggregate SOM, which also includes adsorbed material. Thus, SOM_{occ} has smaller N:C and P:C ratios than total microaggregate SOM. In their study of the uptake of a local spike of $^{14}CO_2$ by a forest ecosystem, Swanston *et al.* (2005) showed that topsoil HF SOM took up ^{14}C more quickly than the occluded SOM. This is expected because the MRT of SOC_{occ} is longer than that of three of the adsorbed pools, i.e. $k_{occ} < k_{\pm,wkads}$, $k_{2,wkads}$, $k_{\pm,strads}$ (Table 1). The $^2 SOC_{strads}$ pool would have been unresponsive to the $^{14}CO_2$ spike.

Hypoxically-protected SOM

The SOM_{hypox1} and SOM_{hypox2} pools are assumed to have the same stoichiometry as SOM_{free}, but lower turnover rates, and this is sufficient to match the observed stoichiometries of soils eith large %C (Figure 2). The other important factor is assumed variation in $\rho_{free,hypox}$, which

allows the model to simulate the wide range of C pools at large %C (Figure 2). This variation in bulk density might reflect differences in the source vegetation (Chambers *et al.*, 2011) or hydrological factors (Holden *et al.*, 2004).

Classification of soils in multivariable matching showed that most of the organic soils in the database were acid (Figure S3). The acidity from the large concentration of organic matter and low base cation weathering input might contribute to the slow turnover of SOM in organic soils. Low pH might reinforce hypoxia in soils that are not permanently waterlogged, by promoting aggregation of SOM through decreasing its net (negative) charge, favouring hydrophobic interactions and consequent aggregation.

How are the model pools related to humic substances?

Much of what is known about the molecular composition of SOM has come from studies of humic substances (HS), defined in terms of their extraction from soil (Hayes & Swift, 2017); some fulvic acid is extracted with acid, but most of the fulvic acid and all the humic acid are released by treatment with a base. The total amount extracted is usually more than half the total SOM. Each of the pools identified in our model (Figure 1) could supply HS, which must therefore comprise a mixture of molecules with different stoichiometries and ages, with appreciable differences among soils.

Stoichiometric data for soil HS, compiled by Rice & McCarthy (1991), give an average N:C ratio of 0.057 for fulvic acids ($n = 127$) and 0.065 for humic acids ($n = 215$), which are similar to the average ratio of 0.061 (standard deviation 0.023) obtained from our 5000 simulations. Therefore, with respect to N:C ratio, HS appear to be representative of bulk SOM, at least on average.

The long-held view that humic substances are the products of *de novo* (bio)synthesis from plant and microbial components has recently been questioned (Kelleher & Simpson, 2006; Lehmann & Kleber, 2015), although such questioning is disputed (Piccolo, 2016; Hayes & Swift, 2017). Humification reactions might occur during the residence of SOM in the different pools, and reactions among mineral-adsorbed molecules have been suggested (Shindo & Huang, 1982; Lambert, 2008; Johnson *et al.*, 2015). It is conceivable that the most strongly adsorbing compounds (in $^2 SOM_{str}$) are relatively large molecules formed *in situ*, but these might not be extracted as HS.

Application and development of the model

The introduction of temperature dependence of metabolic transformations would permit a fuller application to global soils; although the predicted trends align with global data (Figure S2), the smaller range of %C values was not covered, possibly reflecting faster SOM turnover because of higher temperatures at some locations. Another extension would be to modify or elaborate the parameterization to simulate DOM leaching fluxes and stoichiometry. Effects of pH might be introduced with respect to both decomposition rates (Walse *et al.,* 1998; Leifeld *et al*., 2008) and adsorption (see above).

Our modelling approach works satisfactorily because it deals with processes on medium to long timescales, that can be represented physicochemically, approximated by steady state, and with simple and available input data. Short-term OM processing is largely confined to the fast turnover pool, SOM_{free}, with smaller contributions from the 20- and 100-year pools, and nearly negligible involvement of the passive pools. To elaborate the short-term processing, more fully interlinked C, N and P cycling would be required, including plant

growth and death, and the passage of elements through soil microbiota. This might allow the production of $\pm$DOM, and especially ^{2} DOM, to be related to the soil nutrient status.

Although steady state modelling aids understanding, a dynamic model is needed to take into account the effects on topsoil SOM of historical and future changes in temporally-varying SOM factors such as fertilizer applications, atmospheric deposition, N fixation, land use and management changes, climate change and 'black carbon' incorporation. This will require the full coupling of element cycles, and account to be taken of tillage and the weathering processes that affect P supply and soil pH. The inclusion of MM in the model opens the way to include physical erosion. A complete model requires SOM in deeper soil to be represented. The adsorptive selection of ^{2} SOM type materials might be a common process at all soil depths, given widespread observations of increasing N:C and P:C with depth in soil (Batjes, 1996; Rumpel & Kögel-Knabner, 2011; Tipping *et al.*, 2016), and also increasing SOM radiocarbon age with soil depth (Scharpenseel, 1993). For accumulating peat soils, an additional flux needs to be included, namely the continual accumulation of SOM in the deepening catotelm.

Implications for the promotion of SOC storage

According to Whitmore *et al.* (2015) soil carbon pools might be increased by (i) increasing the rate of input of organic matter, (ii) decreasing decomposition rates, (iii) increasing stabilization by physicochemical protection and (iv) increasing the depth of soil in which maximun sequestration occurs. The simulations of Figure 6(a,b) show how possibility (i) might operate. For a fixed topsoil depth, the resulting additional stored SOC would be primarily in the $\pm$SOC$_{ads}$ forms because the strong sites are saturated in most cases (Results).

The MRT of the additional SOC would be 20 years, therefore after a new steady state was achieved the greater input rate of litter would need to be maintained, or else the sequestered C would be lost fairly rapidly over several decades (Tipping *et al.*, 2017).

The present model does not offer a way to change loss rates, as in possibility (ii), but this might be achieved effectively by diverting adsorption of ²DOM to unoccupied strong adsorption sites in MM from deeper soil, a combination of (iii) and (iv). This might be achieved by deep ploughing (Alcántara *et al.*; 2016). In principle, the 'engineering' addition to soils of MM with strong adsorption capacity, could lead to the stabilization of ²SOM, perhaps reinforced by the establishment of plants that produce large amounts of ²DOM. With regard to organic soils, the priority is to conserve the SOC that has already accumulated by ensuring that hypoxic conditions are maintained, or by managing them to promote greater hypoxia.

Conclusions

Temperate soils vary widely in their pools and concentrations of SOC, SON and SOP, and in their radiocarbon contents. There are strong bivariate relations among these variables and related derived variables, with appreciable, but well-defined, data scatter. The data patterns can be reproduced by a steady-state model that recognizes SOM in different physical forms (free, occluded in aggregates, adsorbed, present in hypoxic zones) with different element stoichiometries, and with mean residence times ranging from 1 to 2000 years. The principal controlling factors of SOM properties are the input rate and element stoichiometry of litter,

the DOM adsorption properties of mineral matter, the propensity of the soil to develop hypoxia, and the bulk density of free SOM.

The results support the key modelling assumption, which is that SOM and DOM exist in two stoichiometric forms; an ± form relatively poor in N and P, and a ² form that is relatively rich in these elements. Likely candidates for the N- and P-containing molecules in ² SOM are peptides and inositol phosphates, but some of the ² DOM molecules contain neither element. One form of highly stable SOM arises from the strong selective adsorption of ² DOM by mineral matter. In mineral soils, most of the SON and SOP are in this form, and therefore hardly contribute to nutrient cycling. Most ±SOM exists in pools with mean residence times between one and 100 years; these are free SOM, and SOM weakly adsorbed by mineral matter, occluded within microaggregates, or in weakly hypoxic zones. Highly stable ±SOM occurs in organic soils with strongly hypoxic zones.

The modelling approach is given credence by independent tests. These are (i) agreement between predictions based on British soils with observations from the global WISE database, (ii) similarities between observed temporal variations in bulk soil ^{14}C at four temperate sites and variations predicted by the model for soils with similar properties, (iii) a sensible sequence of average litter inputs in relation to land use (arable < intensive grassland < heath–rough grassland ~ woodland) and (iv) significant and quantitatively sensible relations between observed clay and clay + silt soil pools and simulated adsorption capacity pools.

The steady-state model is the basis for the development of a dynamic version, suitable for simulating changes in SOM through time. It provides insight into how the sequestration of

C in soils might be promoted; for example (i) increasing litter inputs is likely to increase only the more moderately stable SOC pools and (ii) facilitating the adsorption of ² DOM by mineral matter from deeper soil could lead to long-term stabilization.

Supporting information

Model equations.

Excel workbook for model calculations.

Table S1. Litter input rates to soil (gC m^{-2} year^{-1}).

Table S2.Optimization details.

Table S3. Observed and selected simulated results for four locations with temporal radiocarbon data. Figure S1(a–d). Observed data compared with simulations, for different fixed parameter and input values.

Figure S2. Data for global topsoils compared with model outputs from the present study.

Figure S3. Measured pH values for mineral, mineral-organic and organic simulated soils.

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Table 1. Parameters and their values. Fitted values are in bold italic.

Parameter	Symbol	Units	Value
Loss rate constant $\pm SOC_{free}$	k_{free}	year^{-1}	1.0
Loss rate constant $\pm SOC_{occ}$	k_{occ}	year^{-1}	0.01
Loss rate constant $\pm SOC_{hypox1}$	k_{hypox1}	year^{-1}	0.05
Loss rate constant $\pm SOC_{wkads}$	$k_{\pm,wkads}$	year^{-1}	0.05
Loss rate constant $^2 SOC_{wkads}$	$k_{2,wkads}$	year^{-1}	0.05
Loss rate constant $\pm SOC_{strads}$	$k_{\pm,strads}$	year^{-1}	0.05
Conversion factor, $\pm SOC_{free}$ to $\pm SOC_{occ}$	$k_{free,occ}$	m^2 gC^{-1}	1.0×10^{-6}
Fraction of DOM flux that is ^{2} DOM	f_2	-	*0.0658*
Fraction of adsorption capacity that is strong	f_{str}	-	*0.251*
Bulk density of SOM$_{occ}$ and SOM$_{ads}$	$\rho_{occ,ads}$	g cm^{-3}	*0.139*
Bulk density of MM	ρ_{MM}	g cm^{-3}	*1.84*
Fraction of OM is C	f_C	-	0.55
Total soil volume	V_{soil}	cm^3	1.5×10^5
Maximum volume fraction due to $\pm SOM_{hypox1}$	$f_{hypox1,vol}$	-	0.333
Fraction of $\pm SOM_{free}$, $\pm SOM_{occ}$, $\pm SOM_{hypox1}$ converted to DOM	$f_{SOM,DOM}$	-	*0.368*

Table 2. Model input variables and their values. Fitted values are in bold italic.

Input variable	Symbol	Units	Values	
			Lower	Upper
Litter input flux	C_{influx}	gC m^{-2} year^{-1}	50	800
Loss rate constant ±SOC$_{hypox2}$	k_{hypox2}	a^{-1}	0.0005	0.0015
Loss rate constant ² SOC$_{strads}$	$k_{2,strads}$	a^{-1}	0.0005	0.0015
Fraction of non-SOM$_{free}$ volume that is hypoxic	f_{hypox}	-	0.2	0.995
N:C ratio of ±SOM & ±DOM		g g^{-1}	0.0165	0.0495
P:C ratio of ±SOM & ±DOM		g g^{-1}	0.0006	0.0018
N:C ratio of ² SOM & ² DOM		g g^{-1}	*0.0709*	*0.213*
P:C ratio of ² SOM & ² DOM		g g^{-1}	*0.0165*	*0.0495*
Adsorption capacity of mineral matter	σ_{MM}	gC g^{-1}	0.010	0.200
Bulk density of free and hypoxic OM	$\rho_{free,hypox}$	g cm^{-3}	0.05	0.15

Table 3. Model fitting results for (a) bivariate (y against x) relations and (b) average values. All the bivariate relations are significant ($P < 0.001$).

(a)			Observed			Simulated		
y	*x*	*n*	Slope	Intercept	*R*	Slope	Intercept	R
BD	Log$_{10}$	835	−0.928	1.56		−0.926	1.50	
	%C				−0.909			−0.986
Log$_{10}$ %N	Log$_{10}$	835	0.754	−0.943		0.810	−1.06	
	%C				0.954			0.895
Log$_{10}$ %P	Log$_{10}$	66	0.757	−1.87		0.728	−1.86	
	%C				0.492			0.575
Tot C pool	Log$_{10}$	835	6910	1093		5100	2400	
	%C				0.599			0.857

Log$_{10}$ %P	Log$_{10}$	66	0.986	−0.917		0.899	−0.908	
	%N				0.697			0.722
N:C	Log$_{10}$	835	−0.0526	0.120		−0.0708	0.124	
	%C				−0.770			−0.561
P:C	Log$_{10}$	66	−0.0179	0.0258		−0.0181	0.0252	
	%C				−0.661			−0.596
Log$_{10}$ P:C	Log$_{10}$	66	2.44	0.749		1.84	0.145	
	N:C				0.895			0.745
Tot C pool	N:C	835	−131 000	16 800	−0.466	−72 000	11 300	−0.432
Tot C pool	P:C	66	−304 000	8880	−0.499	−282 000	9500	−0.454

(b)	n	Observed	Simulated
Bulk ^{14}C 1980, pMC	–	110.0	111.6
Bulk ^{14}C 2010, pMC	95	102.1	103.2
%C in HF, mineral soil	20	85.0	79.0
Log$_{10}$ %C 5%ile	835	0.255	0.137
Log$_{10}$ %C 95%ile	835	1.71	1.50

Table 4. Explanations of simulated bivariate trends and data scatter in Figure 2.

2(a), 2(b) Slopes of $\log_{10}$ %N against $\log_{10}$ %C and $\log_{10}$ %P against $\log_{10}$ %C are less than 1. When %C is small, there is a large proportion of ² SOM$_{strads}$, which has large N:C and P:C. At large %C, ±SOM dominates, and the N:C and P:C ratios are small.
2(a), 2(b), 2(j), 2(k) Scatter in plots of $\log_{10}$%N against $\log_{10}$ %C, $\log_{10}$ %P against $\log_{10}$ %C, N:C against $\log_{10}$ %C and P:C against $\log_{10}$ %C. Soils can have the same %C, but differ in %N and %P because the SOM comprises different mixtures of ± and ² forms. The range of P:C between ±SOM and ² SOM is greater than that of N:C, hence there is wider scatter in the plot of $\log_{10}$ %P against $\log_{10}$ %C .
2(g) Variation of BD with %C. As %C increases, %MM decreases and SOM, which has low bulk density, increasingly occupies the soil volume.
2(d) The 'trumpet' shape plot of the C pool against $\log_{10}$ %C. At small %C, SOM is mainly SOM$_{occ}$ and SOCM$_{ads}$, and the BD is directly related to the proportions of SOM and MM, so there is a tight relation between the C pool and $\log_{10}$ %C. At large %C the SOM is dominated by SOM$_{hypox1}$ and SOM$_{hypox2}$, which have a range of BDs, hence the C pool – $\log_{10}$ %C relation is looser.
2(h), 2(i) Triangular shapes of the plots of N pool and P pool against $\log_{10}$ %C. When %C is small, so are the C, N and P pools. When it is large, the SOM is dominated by ±SOM, which has small N:C and P:C ratios, and therefore the N and P pools are small. In between, soils vary in their ±SOM to ² SOM ratios giving rise to a range of N and P pools. The spread in N pool values at large %C reflects variations in SOM BD, as in 2(d); this is not evident in the P pool because ±SOM is very low in P.
2(e), 2(f) Large scatter in C pool against N:C and P:C plots. This arises firstly because the N:C and P:C ratios are variable, and secondly because of the range of the ±SOM BD.
2(c), 2(l) trend and scatter in $\log_{10}$%P against $\log_{10}$ %N, and $\log_{10}$ P:C against $\log_{10}$ N:C. The trends are due to the larger N:C and P:C ratios in ² SOM compared to ±SOM. The scatter arises because within ±SOM, or within ² SOM; N:C and P:C do not covary.
2(m), 2(n), 2(o) Radiocarbon trends and scatter. The (weak but significant) positive slopes of the plots of ^{14}C against %C and ^{14}C against SOC pool are due to the large

proportion of the major SOM form, ^{2} SOM$_{strads}$ (highly stable, small ^{14}C), at small %C and SOC pool, and the smaller proportion of the major SOM form, ±SOM$_{hypox2}$ (also highly stable, small ^{14}C), at large %C and C pool. For the same reason, ^{14}C decreases with N:C. The scatter arises mainly from the ranges of $k_{2,strads}$ and k_{hypox2} (Table 2).

Figure 1. Model C pools and fluxes for (a) mineral soils and (b) organic soils. DOC, dissolved organic carbon; hypox1, hypoxically-protected type 1; hypox2, hypoxically-protected type 2; occ, occluded; SOC soil organic carbon (types ± and ^{2}); strads, strongly adsorbed; wkads, weakly adsorbed; xs, excess. The horizontal arrows indicate losses from the system, which can be as CO_2 or DOC.

Figure 2. Bivariate relations plotted for observed (black points) and simulated (grey points) data. A few large C pool values are cut off in panels (d), (e) and (f). Element ratios are in g g^{-1}.

Figure 3. Variation of bulk soil ^{14}C over time, for sites in (a) New Zealand (Judgeford), (b) Great Britain (Meathop Wood), (c) Russia (Kamennaya) and (d) Sweden. The simulated values (lines) are the averages of the three soils that are most similar to the observations (points). See Table S1 (Supporting Information) for element and bulk density data.

Figure 4. Distributions of simulated (a) C, (b) N, (c) P and (d) volume over SOM pools, for different %C values, averaged over 95–105% ranges (i.e. 0.95 to 1.05 , 23.75 to 26.25 %C and so on). Note that the averaging involves results for both mineral and organic soils.

Figure 5. Model pools and fluxes for (a) mineral soils and (b) organic soils. Values in bold are average simulated SOC pools (g m^{-2}), those in italic are average simulated C fluxes in g m^{-2} year^{-1}. Mean residence times of the pools are encircled. Outputs from the adsorbed pools (not shown) are the same as the inputs. See Figure 1 for key to abbreviations.

Figure 6. Dependence of simulated SOC pools on litter input and adsorption capacity, for fixed parameters and averages of other input variables (Tables 1 and 2). Mineral soils: in (a) and (b) the adsorption capacities are 0.05 and 0.15 gC gMM^{-1}, respectively, in (c) the litter input is 425 gC m^{-2}. Organic soils: in (d) the volume available for hypoxia is 25% of the total, in (e) it is 75%. Note that in (d) there is no formation of SOC$_{hypox2}$. In both (d) and (e) the adsorption capacity is 0.1 gC gMM^{-1}.

Figure 7. Plot of simulated adsorption capacity (σ_{MM}) against measured clay+silt content of the soil MM for 56 soils from Toberman *et al*. (2016), after multivariable matching. The reduced major axis regression line has a slope of 0.23 gC g^{-1} and an intercept of –0.022 gC gMM^{-1}, with $r = 0.39$, $P < 0.01$.

(a)

(b)

Adsorption capacity / gC gMM^{-1}

Clay+silt / g gMM^{-1}