Modelling Recalcitrant Soil Organic Carbon, the 'Holy Grail' in Soil Science

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Abstract: Conceptual models of soil organic carbon (SOC) dynamics usually include a pool that is assumed to be resistant to chemical and biological degradation. Such pools, often defined arbitrarily in terms of an age, either finite or 'near-infinite', are needed to accommodate the great stability of soil organic matter (SOM), and can represent more than half the SOM. There is a tendency to include this fraction in SOM models but to specify neither its nature nor its rate of formation. In some computer simulation models, the recalcitrant soil organic matter fraction may even be a 'user-defined' fraction. The recalcitrant pool has been defined in numerous ways in SOM models and now needs to reflect present knowledge of the recalcitrant fraction more closely. This paper examines the 'concept' of the recalcitrant organic matter pool in SOM models, and discusses some of the problems of modelling a soil carbon pool that turns over extremely slowly. These problems must be addressed if we are to formulate more rigorous models that make sense of the extreme stabilization and build up of organic matter. It is anticipated that such models could lead to experimentally verifiable SOM pools. Some of the issues dealt with in this paper relate to problems of modelling in general.

Keywords: Soil-carbon turnover models; Recalcitrant organic matter

1. INTRODUCTION

A large source of uncertainty in the present understanding of the global carbon cycle is the identity, role, distribution and dynamics of the very 'stable' organic carbon in the soil organic carbon reservoir that is degraded slowly, on timescales from centuries to millennia. A knowledge of the proportion and variability of soil C with extremely slow turnover times is required to determine the global inventory of active soil organic matter (SOM) and whether soils behave as sources or sinks of atmospheric CO_2. It is also necessary to examine the long-term effects of climate and land-use change on soil C storage. To this end, mathematical models of soil organic carbon (SOC) dynamics have been useful.

Conceptual models of SOM dynamics usually include a pool assumed to be resistant to chemical and biological degradation and referred to as 'inert', 'almost inert', 'virtually inert and immobile', 'stable', 'refractory', 'inactive', 'passive', 'recalcitrant' or 'dead'. There is a tendency to include such C pools in SOM models but to specify neither their nature nor their rate of formation. These pools, often defined arbitrarily in terms of age as either finite or 'near-infinite', can represent as much as half the SOM. Although recent candidates of recalcitrant carbon are often equated in terms of conceptual pools, the properties of the recalcitrant carbon fraction itself, unfortunately, do not correspond to the properties of the recalcitrant carbon pool assumed in conceptual models. In some computer models of SOM dynamics, the recalcitrant SOM fraction is even reflected as a 'user-defined' fraction. The recalcitrant SOM fraction has been referred to as the 'holy grail' in soil science, with the notion its very existence is defined in terms of models.

This study examines some limitations of modelling the very old turnover SOM fraction. These limitations must be addressed if we are to formulate more rigorous models of the extreme stabilization and build up of organic matter. It is anticipated that such models could lead to experimentally verifiable SOM pools.

A primary aim is to present evidence of the recalcitrant soil carbon fraction and how it has been reflected in mathematical, conceptual and computer-simulation models. A secondary aim is to relate this to general problems faced in simulation modelling. In a companion paper, the equations for estimating recalcitrant SOM fraction in the Rothamsted soil-carbon turnover model, known as the inert organic matter (IOM) fraction from thermonuclear 'bomb' ^{14}C, is examined specifically, as an example of a model of recalcitrant soil organic carbon.

2. CANDIDATES FOR RECALCITRANT SOM

Physical and chemical fractionation, together with radiocarbon (^{14}C) dating, indicates that the surface horizons of most soils contain a very stable 'inert' C fraction with ^{14}C ages of several millennia. The existence of a very old fraction was initially deduced from SOM ^{14}C dates and later from changes in ^{13}C natural abundance. Various factors have been proposed to explain the possible movement of this stable fraction and its resistance to decomposition. These factors include: i) its chemical nature, and protection by clay minerals [Theng et al., 1986]; ii) its physical form [Skjemstad et al., 1996]; iii) its distribution in the soil profile and position within the soil matrix [Tisdall and Oades, 1982]; iv) the soil chemical environment [Oades, 1988]; and v) the maturity of soil [Trumbore, 1996]. The recalcitrant soil organic matter fraction has generally been presumed to consist of a single type or class of compounds. Recent experimental work, however, suggests that in certain soils, a recalcitrant organic matter fraction occurs in, and is associated with, fine particle size fractions.

Candidates for a recalcitrant soil organic matter fraction include i) humified products with a slow turnover rate (> 200 years) inside microaggregates (< 20 μm) [Skjemstad et al., 1993]; ii) a 'discrete', trapped interlayer clay-organic complex isolated from soil particles (< 2μm), with ^{14}C ages much greater than that of externally bound C and of the bulk soil-C [Theng et al., 1992; Torn et al., 1997]; iii) an 'inert' lipid fraction that carries information about its specific origin (e.g. plant, bacteria or algae), and indicates ^{14}C ages (> 10 000 years) for the development of vegetation and soil pedogenesis [Bol et al., 1996]; iv) finely divided charcoal or 'charred' organic matter, which is recalcitrant and can be of any age, with some soils containing up to 30% of soil C as charcoal [Skjemstad et al., 1996]; v) geologically ancient coal; and perhaps vi) a chemically recalcitrant but unstable C compound from undecomposed (unoxidised) lignin and hydrolysable carbohydrate from plants [Sanger et al., 1997]. Other candidates for the recalcitrant soil organic matter fraction in soils have simply been assumed to be peats, carbonates and glass not engaged in biological turnover.

3. MODELLING RECALCITRANT SOM

3.1 The Physical Models

The identity, age and quantity of a biologically inert soil fraction that equates with the recalcitrant SOM fraction of soil C turnover models is needed in studies of soil nutrient cycling, soil-atmosphere interaction [Post et al., 1995], ^{14}C dating of soils [Scharpenseel, 1971], palaeobiology [Bol et al., 1996], soil aggregate formation, charcoal formation [Skjemstad et al., 1996], terrestrial sediment geochemistry, and fossil fuel precursors [Newman and Tate, 1991].

Despite mechanisms being proposed to explain the extreme stabiliy of recalcitrant C in some soils, the age, identity and quantity of this fraction have not been clearly established. Consequently, there are difficulties with how SOM models reflect this fraction and how one models a fraction we cannot measure and understand little about.

3.2 The Model's Assumptions

There are numerous current models of SOM dynamics [e.g. http://yacorba.res.bbsrc.ac.uk/cgi-bin/somnet]. They are generally mechanistically based, where factors affecting organic matter turnover, such as clay, soil temperature, soil moisture pH, N content and oxygen availablity, are incorporated as empirically determined equations, from short-term experimental data. Most contemporary SOM models generally include a pool that is i) uncoupled from the system, is discrete and that may or may not reflect 'fossilised' SOM as assumed in the Rothamsted soil-carbon model [Jenkinson, et al., 1992], which has an arbitrary turnover time of 50 000 years; and/or ii) is coupled to the system and has a faster turnover time (> 1000 yr), as assumed in the CENTURY model [Parton, et al., 1989]. The size of these pools, important in calibrating SOM models, is usually determined by total C, clay content, ^{14}C ages or by subtraction of pools from total C.

In computer simultation models, the 'size' of the recalcitrant SOM fraction has been arbitrarily defined as an absolute value across all sites, equated to zero, or excluded. Since the resulting proportion of the non-'inert' pools to total C can be instrumental in determining active C budgets and the balance of C and its rate of exchanges between soil pools, soil and the atmosphere, the size of the possibly significant recalcitrant SOM-C fraction can pose a major limitation on the use of SOM models. In contrast to the IOM-C (inert organic matter) pool of the Rothamsted model, the extremely slow turnover pools in most contemporary models are also often quantitatively very significant, with over half total C assumed to be effectively left out of consideration by model dynamics [Christensen, 1995].

3.3 The Computer Simulation Models

There has been no comparative study of the pools assumed in current computer SOM simulation models, which have very great turnover times. This would be a difficult task, as often only brief descriptions (e.g. 'physically protected OM', 'chemically stabilised OM', 'old C', 'user defined fraction') for the pool may be obtained; and the underlying model assumptions and their formulations are generally not available. Estimates of the size of these pools may be compared, but such studies are limited because these models, only as good as the assumptions and data available, have considerably varying assumptions. These pools are arbitrarily included by the 'modeller', particularly following land-use and management changes, to improve simulation model performance rather than to satisfy well-defined operational concepts, and can be considered parking lots for SOM left over during model calibration. One rapidly comes to the conclusion that "simulation" is a process of experimenting with a computer rather than a process of experimenting with a 'concept'.

The limitations on current SOM simulation models, makes it impossible to test any SOM turnover model or perform a comparative study of SOM models. The inclusion of a slow pool that is arbitrarily fitted to data or is simply a 'user defined' fraction, results in a slow, non-active or passive pool defined in terms of conceptual SOM models.

3.4 The Mathematical Models

Current SOM turnover models of soil C dynamics are usually formulated by assuming a multicompartmental model in which the 'system' is divided into a number of dominant compartments. Transfer of material from one compartment to another is usually assumed to obey first-order rate kinetics. These compartments or 'pools' range from very active pools that have a rapid turnover time to pools that are effectively inert; and there are usually other pools with intermediate turnover times. SOM pools are assumed to be homogeneous and interdependent wholes.

The general solution of an n-compartmental, open, linear, time-dependent, multicompartmental model can be shown to be a sums-of-exponentials (polyexponential) function given by

$$\sum_{i=1}^{n} a_i \exp(\lambda_i t), \tag{1}$$

where the constants a_i, functions of the pool sizes and microscopic rate constants, are called pre-exponential constants, and λ_i, functions of the microscopic rate constants, are the eigenvalues of the system. Such an equation helps identify the number of major pools in a SOM system [Parshotam et al., 2000].

3.5 Model Results or Model Assumptions?

Equation (1) needs not assume a slow turnover fraction but may suggest one from experimental data. It may suggest that a multicompartmental model will be a valid model to describe the system. Contrast this with the *a priori* assumption that a slow turnover compartment exists whose size has to be estimated.

The eigenvalues λ_i in equation (1) may indicate relative turnover times and, although useful, these can mislead and should not be interpreted as estimates of pool decay rate constants or average turnover-rate constants for active, slow and passive pools independent of each other, i.e. discrete. Nor should estimates of pre-exponential constants be interpreted as pool-size estimates. There is greater variation in pool-size estimates than rate constant estimates, and this should be considered when relating pool sizes to soil and environmental conditions. With the exception perhaps of a discrete recalcitrant SOM fraction, treating soil C fractions as independent, undifferentiated 'wholes' may be a gross oversimplification that results in model estimates of a very large passive pool, and with large variations, from equation (1). Widely varying eigenvalues or turnover times imply that pools can be uncoupled and studied independently. ^{14}C data may be used to separate pools with a great turnover time (>1000 yr) from pools with slow turnover times (>100 yr). Various rate constants that characterise the system, e.g. ^{14}C ages and MRTs that are converted to calendar years, turnover times, the half life ($t_{1/2}$) of the terminal decomposition phase, will converge for a fraction with a great turnover time.

3.6 The Conceptual Models. Do Bigger and More Complex Models Give Better Estimates?

There is a tendency today to assume that bigger models mean better models. These simulation models are usually driven by the need for end products for end users, rather than by a desire for a deeper understanding of some of the 'key' processes. Some SOM models, (e.g. CENTURY [Parton, et al., 1989]), although simple in structure, may have up to a thousand modifiers, most of which can be turned off at any one time. Although these models are useful to organise information and simulate the appearence of a likely scenario, sometimes on a global scale, with innumerable runs, it is impossible to deduce the significance of individual model parameter estimates that, like the recalcitrant SOM pool, are mostly free parameters arbitrarily chosen. It is satisfying to include submodels and feedback loops in a model, but more complex models simply require more assumptions; sometimes major. A big model can be made to fit almost any data and should not run ahead of the data available for parameterizing and testing it. Usually, only total C data are available, and unless steady state conditions are assumed, only single-compartment SOM models are possible.

4. DISCUSSION

4.1 Why Model Recalcitrant SOM?

There are current limitations that do not allow the modelling of inert C to be very practical. First, and most important, there are several candidates for recalcitrant SOM and it is important to define this fraction more clearly before it can either be modelled and surrogate relationships derived to estimate its size or be related to an experimentally verifiable 'isolated' pool in SOM models. Second, although simple methods are currently being developed to measure the size of a candidate for inert fraction on a routine basis, inaccurate measurement and the lack of any definite surrogate relationships with soil physical and chemical properties to estimate its size still mean that it either has to be excluded from soil C models altogether or included in the larger slow cycling fractions. Third, if the biologically recalcitrant SOM fraction is an identified, measurable and isolated discrete fraction but is associated by its nature with 'ultimate' mineral particles, its size would depend not only on soil properties and particle fractions associated with it but on the type of physical or chemical fractionation (e.g. the various acid hydrolysis treatments) involved and the energy expended in isolating it. That is, it appears as if the recalcitrant SOM fraction and the recalcitrant SOM pool are operationally defined. Fourth, it has been suggested that since charcoal is determined as organic C by conventional methods, it is essential for SOM models to contain this pool. However, if the inert fraction is a result of the (unknown) history of the system (recent charcoal from burning, etc.) it may not be meaningful to define it in terms of an age, to find surrogate relationships and to include it in dynamic models; the presence in many allophanic soils of finely divided charcoal can actually complicate the estimation of the recalcitrant SOM fraction. Finally, if the recalcitrant SOM pool somehow reflects an ultimate (but not necessarily discrete) small physical fraction of SOM representing an integration of accumulation that either has long reached a steady state or continues to accumulate slowly, playing an insignificant and barely persisting role in SOM dynamics, it may not be necessary to include it in models of SOM. All the above points suggest that recalcitrant SOM acts as a signature for environmental history and, depending on its definition, may be isolated, modelled and compared across sites, but not necessarily included in SOM models.

4.2 Model Simplification

If it is the aim of science to present the facts of nature in the simplest and most economic conceptual formulations, then the best model is not necessarily the most complex, nor the one of which overtly reflects the most sophisticated understanding of the system. It is often the case that as a model is refined, it becomes simpler, but this process can take many years. As some information is likely to be superfluous, simplifying a model may be necessary, and here the analytical solution is useful for lumping pools or collapsing a system [Sinha and Kuszta, 1983].

A 'bigger meaning better' approach in SOM turnover modelling does not allow the dominant processes of a system to be revealed. Consequently, this cannot lead to a scientific paradigm shift in our understanding of recalcitrant SOM. One need not measure everything in one's path to prove that things have size. A simple correlation between total C and clay content gives much useful information about SOM stabilization.

4.3 Is the 'Concept' of Recalcitrant SOM Independent of the 'Concept' of SOM?

The extremely slow C pool in soils is not as closely linked to the nutrient cycles as the more rapidly turning over C pools and is independent of seasonal variations, inter-annual variations and land use. This inherent property of recalcitrant SOM fraction is useful to define recalcitrant SOM fraction but is not useful to determine how climate and land-use control the long-term accumulation of recalcitrant SOM-C. For this, the *whole* system must be examined. The long-term effects of climate and land-use change on soils cannot be determined from a pool independent of the active pools. This is the case whether the inert fraction is or is not discrete, is controlled by or is a consequence of environmental factors or is even reflected by a pool included in the larger slow pools. The recalcitrant SOM and slow pools may be considered to be reserves that take time to replace and are used only when active C is used up. The effects of climate and land-use change the active cycling pool. This in turn, changes the proportion that is recalcitrant SOM. Since SOM retains a long-term memory of past global or regional environmental changes, as well as associated landscape dynamics that have occurred during pedological development, the ^{14}C and C content of very old C in relation to *whole* soil ^{14}C and bulk SOM, provides a useful clue to environmental history [Bol et al., 1996]. The origins of organic matter inputs to soils and sediments can also be inferred by chemical differences in old C [Sanger et al., 1997]. Although existing models of SOM dynamics operate over months to centuries, it is not clear whether these models will adequately forecast response to future impacts: temperature changes pool sizes with little effect on pool rate constants [Zogg et al., 1997], and decomposition of the recalcitrant pools of SOM may be as sensitive to changes in temperature as the labile pools [Townsend et al., 1995].

5. RECOMMENDATIONS

Future models are likely to involve mechanisms, the representation of a real process in terms involving familiar physical actions. Mathematical models involving recalcitrant SOM should deal with mechanisms responsible for extreme stabilization such as physical protection. When possible, observations (which include 'experiments') must take first place in modelling recalcitrant SOM. Experiments must be better designed to isolate mechanisms of extreme stabilization. Conceptual models of SOM stabilization mechanisms and their controls can provide a basis for mathematical (i.e. quantifiable) models. Existing data from soil chrono-, topo- and climo-sequences must be utilized to test these mechanisms. Since recalcitrant SOM does not participate actively in SOM dynamics, it is unlikely to play a useful role in SOM models. However, it is quite likely to become a useful index for SOM formation, recalcitrance, interactions, accessibility and stability and their mechanisms.

Future representation of the spatial variability of recalcitrant SOM in SOM models should rely on soil attributes that are easily measured or commonly held in databases, rather than on expensive ^{14}C measurements. To identify such attributes and determine surrogate relationships, more rigorous models will be needed with well-defined operational concepts that can be experimentally verified. Soil ^{14}C measurements help identify common soil attributes that control IOM-C, but are unlikely to be used directly or extensively for this purpose.

The approach of modelling seen in this work challenges mathematical modelling in many ways. Obviously, there are numerous ways of formulating a SOM model mathematically, as a means of testing recalcitrant SOM stabilization mechanisms and of generating new hypotheses. Mathematical models of SOM should be developed so they can be tested and based on well-founded mathematical principles. Mathematics should be used to illuminate the mechanisms, rather than the mechanisms illuminating mathematics. Mechanisms are more important than mathematical equations. Once the mechanism is identified, fitting it out with suitable mathematics is often the easier task. There is no unique and absolute SOM model towards which we should be converging or for which we should be gathering data to validate. The belief that mathematics carries the truth and that the physical world must somehow conform to the theory, is to invert the process of scientific discovery!

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