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Are oxygen limitations under recognized regulators of organic carbon turnover in upland soils?

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- ## Abstract

Understanding the processes controlling organic matter (OM) stocks in upland soils, and the ability to management them, is crucial for maintaining soil fertility and carbon (C) storage as well as projecting change with time. OM inputs are balanced by the mineralization (oxidation) rate, with the difference determining whether the system is aggrading, degrading or at equilibrium with reference to its C storage. In upland soils, it is well recognized that the rate and extent of OM mineralization is affected by climatic factors (particularly temperature and rainfall) in combination with OM chemistry, mineral-organic associations, and physical protection. Here we examine evidence for the existence of persistent anaerobic microsites in upland soils and their effect on microbially mediated OM mineralization rates. We corroborate long-standing assumptions that residence times of OM tend to be greater in soil domains with limited oxygen supply (aggregates or peds). Moreover, the particularly long residence times of reduced organic compounds (e.g., aliphatics) are consistent with thermodynamic constraints on their oxidation under anaerobic conditions. Incorporating (i) pore length and connectivity governing oxygen diffusion rates (and thus oxygen supply) with (ii) 'hot spots' of microbial OM decomposition (and thus oxygen consumption), and (iii) kinetic and thermodynamic constraints on OM metabolism under anaerobic conditions will thus improve conceptual and numerical models of C cycling in upland soils. We conclude that constraints on microbial metabolism induced by oxygen limitations act as a largely unrecognized and greatly underestimated control on overall rates of C oxidation in upland soils.

Keywords

Soil carbon Organic matter Anaerobic metabolism Soils Oxygen limitations

List of symbols

$f_{anaerobic}$

'Anaerobic fraction', anaerobic proportion of the overall pore space

r_{oxygen}

Scaling factor that describes the effect of oxygen limitations on overall OM oxidation rates (ranges from 0 to 1)

F_t

Thermodynamic driving force for the oxidation of a carbon compound coupled to the reduction of a given terminal electron acceptor. It varies from 0 (reaction inhibited) to 1 (reaction occurs at maximum rates) and can be estimated based on NOSC

NOSC

Nominal oxidation state of carbon can be calculated for any given compound based on its stoichiometry (LaRowe and Van Cappellen [2011](#))

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Introduction

Soil plays a critical role in global carbon (C) cycling, representing the largest dynamic C stock on Earth—3000 Pg of C are stored in soils (Köchy et al. [2015](#)) which is four times the amount stored in the atmosphere. Soil organic matter (OM) quantities are regulated by the balance between plant inputs and losses through microbial OM mineralization (i.e., complete oxidation of organic compounds to CO₂) or export of dissolved OM in a given soil. Fundamental drivers of OM mineralization are principally climatic factors, such as temperature and precipitation, combined with OM chemistry (Cotrufo et al. [2013](#)), the availability of nutrients to the decomposer community (Torn et al. [2005](#); Klotzbücher et al. [2011](#)), the formation of protective associations between SOM and soil minerals such as phyllosilicate clays, but in particularly high surface area, hydrated metal oxides (Oades [1988](#); Torn et al. [1997](#)), and physical protection, which constrains the accessibility of substrates to decomposer organisms (Veen and Kuikman [1990](#); Killham et al. [1993](#)). More recent theories highlight the importance of the whole plant-soil-microbe system (Schmidt et al. [2011](#)) in regulating OM mineralization rate. What remains elusive is to what extent constraints on microbial metabolism imposed by the absence of the most favorable electron acceptor, oxygen, control overall rates of OM mineralization in upland soils.

The disregard for oxygen limitations is surprising given the evidence that the complex physical structure of soils results in an abundance of anaerobic microsites and associated metabolic gradients even within seemingly aerobic, well-drained soils. Although the importance of oxygen limitations on OM preservation is well recognized in marine and lacustrine sediments (Hedges and Keil [1995](#); Hartnett et al. [1998](#); Arndt et al. [2013](#)), wetlands (Silver et al. [1999](#); Freeman et al. [2001](#)), and thawing permafrost soils (Kane et al. [2013](#); Fan et al. [2014](#)), the cumulative impact of such anaerobic microsites on OM mineralization rates and ultimately C storage in upland soils is largely ignored. This knowledge gap is also reflected in the way current C cycling models represent the impact of oxygen availability on OM mineralization rates in soils (Riley et al. [2011](#); Koven et al. [2013](#)); for example, efforts to approximate the oxygen impact on C turnover rely on a scaling factor that was derived from incubation experiments with peat samples.

Here we seek to critically evaluate whether such oxygen limitations within upland soils contribute significantly to the preservation of OM in soils. We specifically aim to (i) document what is known about the extent of anaerobic microsites in upland soils and how they are represented in C cycling models, (ii) describe how anaerobic conditions can impact the kinetics and thermodynamics (and thus the rate and extent) of microbial C oxidation in upland soils, (iii) evaluate whether existing data support kinetic and/or thermodynamic predictions that could be used in modeling framework and (iv) identify future research needs. We focused our discussion on mineral soils in all landscape positions that do not experience periods of water saturation in normal years.

Anaerobic microsites and their impact on OM mineralization in upland soils

Efforts to examine oxygen impacts on soil C cycling have largely been limited to wetlands and hydric soils (Reddy et al. [2000](#); Fiedler and Kalbitz [2003](#); Fiedler et al. [2007](#)), but they have more recently expanded to well-drained tropical forest soils (Silver et al. [1999](#); Liptzin et al. [2010](#)). Aside from a few exceptions (Andersen et al. [1998](#); van der Lee et al. [1999](#); von Fischer and Hedin [2002](#); Fimmen et al. [2008](#)), the spatial and temporal dynamics of anaerobic microsites in upland soils, the factors controlling their formation and persistence, and their impact on soil C cycling have not been studied in great detail.

Formation of anaerobic microsites in upland soils

The physical structure of upland soils (i.e., aggregates and peds) forms a network of redox gradients that exert a dominant influence on the metabolic

diversity of soils (Fig. 1). Macropores ($>50 \mu\text{m}$), with low tortuosity and high pore connectivity, in combination with micropores, with high tortuosity and discontinuity, result in highly-variable flow of gas and water (Jarvis 2007). Transport of gases (e.g., oxygen) and solutes (e.g., nutrients and DOC) through macropores is governed by advection, while diffusion is assumed to be the dominant mode of transport in micropores. If oxygen supply (via diffusion) in the soil matrix is slower than its consumption (via microbial respiration), the interior of structural units (aggregates or peds) becomes oxygen depleted relative to the exterior (macropores) (as seen in Sexstone et al. 1985), leading to gradients in redox potential (Zausig et al. 1993). If these gradients persist, frequently promoted by seasonal water saturation (Jacobs et al. 2002) or a continuous supply of root C (Richter et al. 2007; Fimmen et al. 2008; Hong et al. 2010), they lead to the differentiation of redoximorphic features.

[Open image in new window](#)

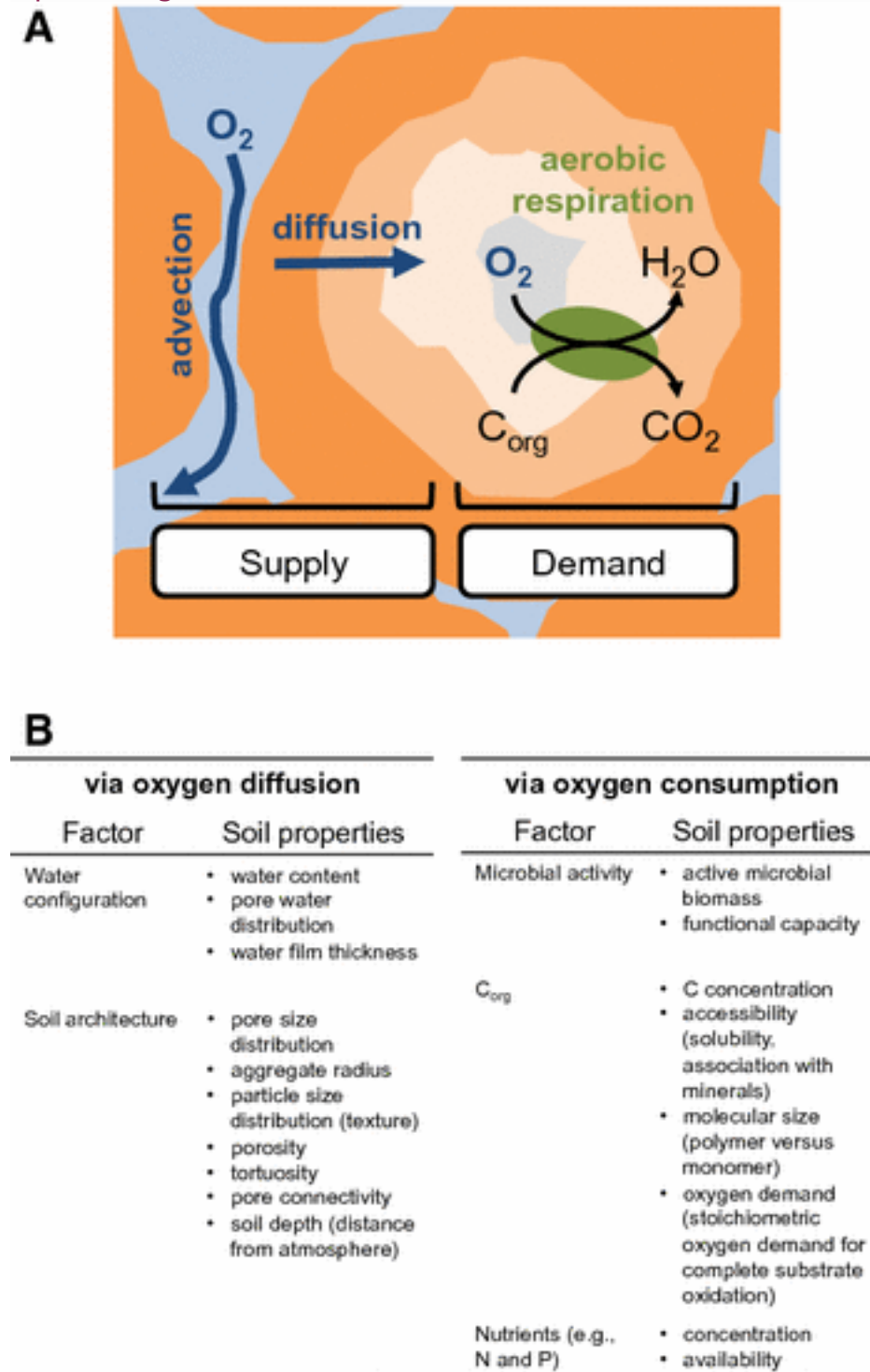


Fig. 1

a Conceptual diagram illustrating the balance between oxygen supply (via advection/diffusion) and demand (via microbial oxygen consumption) responsible for the formation of anaerobic microsites in well-structured upland soils. **b** Factors influencing the oxygen diffusion and consumption in

aggregate domains and soil properties used to quantify the influence of these factors (the reader is referred to the text for a brief description of the ways in which the balance between oxygen supply and demand can be modulated by plant roots)

It is important to note the ways in which roots can contribute to the formation of anaerobic microsites and the development of strong redox gradients in upland soils. Roots can directly reduce soil oxygen concentrations via root respiration (Bidel et al. [2000](#)) or indirectly by stimulating heterotrophic respiration in the rhizosphere (Keiluweit et al. [2015](#); Hojberg and Sorensen [1993](#)) and releasing organic reductants (Fimmen et al. [2008](#); Richter et al. [2007](#)). A detailed description of these processes is beyond the scope of this effort, but the question of how root-mediated modifications of soil oxygen concentrations affect soil C cycling in upland soils is still unanswered and not considered in current model frameworks.

Evidence for anaerobic metabolism in upland soils

Oxygen limitations within the soil matrix prompt microbes to switch to alternative terminal electron acceptors (TEAs), and a diversity of anaerobic metabolic pathways transpire (Hansel et al. [2008](#)). As a result, denitrification (Sexstone et al. [1985](#)), Mn and Fe reduction (Hansel et al. [2008](#); Hall et al. [2013](#)), and methanogenesis (von Fischer and Hedin [2002](#)) can all be detected in seemingly well-aerated upland soils.

Compared to nitrate and Mn reduction, which ensue rapidly even at modest moisture contents (Bartlett [1988](#); Vermes and Myrold [1992](#); De-Campos et al. [2011](#)), the onset of microbial Fe reduction requires prolonged periods of anaerobiosis. Nevertheless, Fe reduction is increasingly recognized as the quantitatively most important anaerobic respiratory pathway in a large range of upland soil ecosystems because of its abundance relative to other TEAs (Schuur and Matson [2001](#); Miller et al. [2001](#); Chacon et al. [2006](#); Fuss et al. [2010](#); Thompson et al. [2011](#); Hall et al. [2013](#)).

Some volcanic soils show redox potentials sufficient for microbial Fe reduction (Schuur and Matson [2001](#)) and Fe(II) formation (Thompson et al. [2011](#)). In humid tropical forest soils, Fe reduction dominates anaerobic respiration in laboratory experiments (Chacon et al. [2006](#)), and Fe(II) was observed at relatively low moisture contents in the field (Hall et al. [2013](#)). Even in well-drained, seemingly oxic spodosols in temperate forests, the soil solution can contain up to 60 % Fe(II) (Fuss et al. [2010](#)). Redistribution of Fe(II) across persistent anaerobic-aerobic interfaces, creating redoximorphic features in the process (Jacobs et al. [2002](#); Richter et al. [2007](#); Fimmen et

al. [2008](#)), provides further evidence for the importance of anaerobic Fe reduction in upland soils.

Upland soils are also inhabited by a surprising number of methanogens that rely on strictly anaerobic conditions. Peters and Conrad ([1995](#)) demonstrated that several types of well-aerated upland soils quickly become methanogenic when incubated under anoxic conditions. Similarly, West and Schmidt ([2002](#)) were able to induce methanogenesis in well-drained alpine soils when incubated under an H₂/CO₂-enriched atmosphere. Teh et al. ([2005](#)) also found methanogenesis occurring in tropical forest soils, Poplawski et al. ([2007](#)) retrieved sequences of methanogens in a well-aerated Swedish barley field, and Lee et al. ([2012](#)) observed growth of methanogens in aerated laboratory incubations. These findings suggest that methanogens not only become active under relatively moist or saturated conditions, but are also active in anaerobic microenvironments within otherwise oxic, upland soils (Angel et al. [2012](#)).

Potential impacts on OM mineralization rates in upland soils

It has long been known that experimentally decreasing bulk oxygen concentrations (either by replacing the headspace with oxygen-free gas or prolonged water saturation of the soil) generally decreases OM mineralization rates relative to fully oxygenated treatments (Greenwood [1961](#); Parr and Reuszer [1962](#); Reddy and Patrick [1975](#)). By contrast, the impact of anaerobic microsites existing within an otherwise well-aerated soil volume on bulk C oxidation rates is not well documented. Using previously published data from two studies we can make a first estimate of the effect. Greenwood ([1961](#)) found that when incubating soil across a range of headspace oxygen concentrations, decreasing bulk oxygen concentration to 25 % saturation resulted in a decrease in C oxidation rates by 71 %. Sexstone et al. ([1985](#)) documented that between 38 and 83 % of a soil ped incubated under fully aerated conditions exhibited oxygen concentrations of less than 25 % saturation. If we assume a reduction in C oxidation rates similar in magnitude to that observed by Greenwood ([1961](#)), oxygen limitations in the soil peds investigated by Sexstone et al. ([1985](#)) may decrease the total potential soil C oxidation rates by up to 27–59 %. This range is in general agreement with comparisons of mineralization rates in anaerobic and aerobic incubations of bulk soil, where anaerobic rates in arable (Devêvre and Horváth [2000](#)) and permafrost soils (Frolking et al. [2001](#); Wania et al. [2009](#)) were 23 to 97.5 % lower than those under aerobic conditions. Although the overall effect likely depends on the experimental conditions and soil characteristics, these measurements serve to illustrate the magnitude to which anaerobic microsites created by soil structure can influence C oxidation rates and thus OM storage.

Slower rates of C oxidation often observed in the interior of peds (Bundt et al. [2001b](#); Amelung et al. [2002](#); De Gryze et al. [2006](#)) provide further evidence for the rate controlling influence of anaerobic microsites. A study of soil C within soil peds conducted by Ewing et al. ([2006](#)) in Californian grassland soils suggests that microbial C oxidation is constrained by oxygen limitations in the ped interior. Turnover time of soil C along the exterior of soil peds (>20 mm), determined by ^{14}C measurement, was faster compared to the matrix (ped interior) under native (structured) conditions (Ewing et al. [2006](#)). Preferential flow paths also show faster turnover of C and N in forest soils (Bundt et al. [2001a](#)) and depletion of C under prairie soils (Amelung et al. [2002](#)) relative to the soil matrix. Combined, these studies suggest that oxygen may have a particularly strong impact on overall C oxidation.

Predicting the anaerobic fraction of upland soils and its impact on overall C oxidation

Recent soil C cycling models have incorporated numerical approximations of the impact of oxygen limitations on C oxidation rates. Models such as the dual Arrhenius and Michaelis–Menten kinetics (DAMM) model (Davidson et al. [2012](#)) or TOUGHREACTv1 (Riley et al. [2014](#)) use comparatively simple functions that link soil C oxidation rates to substrate and oxygen concentrations in a homogeneous soil layer. Another family of models developed approaches to estimate oxygen dynamics within structurally heterogeneous (i.e., aggregated) soil environments (e.g., Currie [1961](#); Smith [1980](#)). What both modeling approaches have in common is their reliance on approximations of the relative balance between *oxygen supply* and *demand* to describe oxygen dynamics in soils. Both treat oxygen supply and demand as a function of the rate of diffusion and microbial oxygen consumption, respectively, which are estimated using basic soil characteristics (Fig. [1](#)).

Models describing oxygen dynamics in a uniform soil environment

As oxygen diffusion in air exceeds diffusion in water by a factor $>10^4$, oxygen supply is commonly estimated by calculating effective diffusion rates using Fick's law of diffusion and basic soil–water content relationships. The DAMM model (e.g., Davidson et al. [2012](#)) relies on air-filled porosity (calculated using bulk density and volumetric water content) to estimate the rate of oxygen diffusion to the site of oxygen consumption. Microbial oxygen consumption is expressed by an on linear biological consumption term based on Michaelis–Menton kinetics, which often describes biological activity. Consequently, the rate of consumption depends on the Michaelis constant and oxygen concentration. The Michaelis constant has to be determined for each soil independently, using simple approximations

(Davidson et al. [2012](#)) or experimentation (Myrold and Tiedje [1985](#)). The dependence on oxygen concentration means that not only oxygen diffusion but also consumption (via heterotrophic respiration) is approximated using air-filled pore space, rather than more direct measures of microbial activity (e.g., CO₂ production).

Davidson et al. ([2012](#)) and Riley et al. ([2014](#)) couple oxygen consumption rates to C oxidation rates using Michaelis–Menton kinetics, in the latter case even incorporating C use efficiency and stoichiometric oxygen demand for the full oxidation of specific substrates to CO₂. The model assumes that C oxidation rates are not limited by oxygen unless the bulk oxygen concentrations are insufficient to meet demands. However, both studies average across entire soil layers at moisture contents that do not predict oxygen limitations at the bulk scale. The question arises if incorporating terms or algorithms representing soil structural heterogeneity into models would result in a model output that predicts the development of anaerobic microsites.

Models describing oxygen dynamics in a structured soil environment

Recent process-based reactive transport models have therefore incorporated different forms of the classic ‘aggregate’ model. This model and its many modifications were designed to (first) calculate an anaerobic fraction ($f_{anaerobic}$) within soil aggregates and (second) apply a scaling factor ($r_{anaerobic}$, discussed in detail below) to account for the resulting decline in oxidation rates.

Currie ([1961](#)) developed numerical expressions describing the radial diffusion of oxygen towards the center of a single soil aggregate. Heterotrophic respiration is assumed to be uniform across the aerated portion of the soil aggregate. Oxygen consumption is taken as directly proportional to heterotrophic respiration and thus constant across the aerobic fraction. Oxygen consumption (via heterotrophic respiration) is considered to proceed uninhibited until oxygen supply drops below a critical threshold (e.g., <5 %, Currie [1984](#)). The model allows calculation of the anaerobic fraction of a given spherical aggregate when the radius of the aggregate, the external oxygen concentration, the diffusion coefficient, and the rate of consumption are all known. Smith ([1980](#)) and Arah and Smith ([1989](#)) extended the single ‘aggregate’ model by explicitly considering aggregate size distribution and diffusion within intra-aggregate pores down the soil profile. The size distribution of aggregate radii is derived from moisture retention curves (small pores which remain saturated at a cut-off tension are concentrated within the aggregates), effective diffusion rates are calculated using air-filled porosity, and tortuosity is assumed to be constant. Oxygen consumption is

first described using Michaelis–Menten kinetics, but then assumed to be constant (simplified to first order kinetics) and deemed independent of substrate, oxygen concentration or location in the aggregate. Again, the model assumes a single oxygen concentration threshold at which all oxygen consumption (via heterotrophic respiration) ceases. Arah and Vinten (1995) contrasted the ‘aggregate’ model with a ‘simple-structure’ model developed by Rijtema and Kroes (1991). The basic assumptions here are very similar to that of the ‘aggregate’ model, but the model is founded on a random distribution of cylindrical air-filled pores equal to the mean of the unsaturated fraction of the pore size distribution. The radii of aerobic zones surrounding the pores in the saturated soil are calculated based on oxygen diffusion and consumption estimates. Diffusion rates within the saturated soil are approximated using single tortuosity factor and consumption rates are again taken as constant (zero-order rate). The part of the soil matrix not included within these (overlapping) aerobic zones is anaerobic. Numerical approximations of the ‘simple-structure’ model provided by Arah and Vinten (1995) have recently been incorporated into process-based soil C cycling models (Riley et al. 2011; Koven et al. 2013) to estimate $f_{anaerobic}$.

The ‘aggregate’ models are informed by the notion of discrete aggregate domains with anaerobic cores and aerobic exteriors, as nicely depicted for peds (albeit in simplistic rendering of micro-scale heterogeneity) by Sexstone et al. (1985) (adapted for Fig. 1). The ultimate goal of these models is to predict the extent of $f_{anaerobic}$ in different soils or for the same soil under different conditions by measurement of the diffusion coefficients, moisture contents, porosity, oxygen consumption rate and aggregate size distribution. However, the predicted $f_{anaerobic}$ has yet to be validated experimentally. It further remains to be seen how well ‘aggregate’ models capture oxygen dynamics, and ultimately the impact on OM mineralization rates, in soils with less discrete ‘aggregate’ boundaries or soils where ‘aggregate’ domains are subjected to seasonal dynamics (e.g., shrink–swell behavior). Revisiting the following assumptions may improve future estimates of $f_{anaerobic}$:

Assumption 1

Effective oxygen diffusion coefficients within aggregate domains can be estimated solely based on porosity. The reliance on air-filled (‘aggregate’ model) or water-filled porosity (‘simple-structure’ model) to calculate diffusion coefficients within aggregate domains disregards variations in pore configuration (e.g., water film thickness, tortuosity and pore connectivity) that lead to varying diffusion lengths. The issue is nicely illustrated by comparing sandy and clay-rich soils, which—assuming the same bulk density and volumetric water content—can have the same air-filled porosity. A model solely relying on air-filled porosity would calculate the same effective diffusion rates for both soils. This assumption also doesn’t consider

that pore size distribution often varies across aggregates of different sizes collected from the same soil (Mangalassery et al. [2013](#)). Pore connectivity and tortuosity within a given soil can be estimated using pore or particle size distribution (or soil texture) (Nielson et al. [1984](#)), which is a parameter that is easily obtained from soil databases. A 'pore model' that calculates diffusion based on pore size distribution obtained by soil-water retention curves at least partly accounts for differences in pore architecture (Nielson et al. [1984](#)). Incorporating parameters such pore and particle size distribution, in addition to or as a function of air-filled porosity, may better constrain estimates of oxygen diffusion and improve model predictions of $f_{anaerobic}$.

Assumption 2

There is a single critical oxygen concentration at which heterotrophic respiration ceases in all organisms within the soil (Currie [1961](#), [1984](#); Smith [1977](#)). This assumption implies that C oxidation only occurs in the aerobic fraction of the soil, ignoring anaerobic metabolism occurring in the anaerobic fraction. Further, abiotic and biotic oxidation of reduced species (e.g., Fe^{2+} , Mn^{2+} , CH_4 and NH_4^+) produced under anaerobic conditions consumes additional oxygen. These reactions are not directly coupled to C oxidation, but can quantitatively contribute to overall oxygen consumption. Integrating anaerobic metabolism and its contribution to C oxidation and oxygen consumption may improve model predictions of aggregate oxygen dynamics. A few attempts have been made to quantify the anaerobic contribution to overall C oxidation in unsaturated soils. Bridge and Rixon ([1976](#)) used respiratory quotients, defined as the ratio of the volumetric rates of carbon dioxide production and oxygen consumption, to infer shifts from aerobic to anaerobic respiration. However, the respiratory quotient was seen to be strongly affected by transport processes, calling into question whether it can serve as a sensitive indicator of the contribution of anaerobic respiration.

Assumption 3

Oxygen consumption is constant throughout aerobic aggregate domains. If the models assume that oxygen consumption is directly proportional to heterotrophic respiration, oxygen consumption is subjected to the same controls, e.g., temperature, nutrient limitations, or substrate chemistry and availability. While C cycling models begin to incorporate these controls on heterotrophic respiration, they have yet to be considered in anaerobic respiration. Moreover, numerous studies provide evidence for the heterogeneous distribution of microbial activity in upland soils (Mateos and Carcedo [1985](#); Navarro-García et al. [2012](#); Bailey et al. [2012](#); Smith et al. [2014](#)). Assuming uniform heterotrophic respiration across aggregate domains does not account for the formation of 'hot spots' with greater C availability and microbial activity, which exist in association with

macropores, roots, or organic residues ('biopores') known to cause strong redox gradients (Fischer et al. 1989; van der Lee et al. 1999; Fimmen et al. 2008). Finally, this assumption also excludes cases in which oxygen consumption varies with time as a result of changing oxygen or substrate availability, as would be the case during periodic rainfall events.

Estimating the impact of anaerobic conditions on C oxidation rates
 Once $f_{anaerobic}$ is calculated, traditional models of soil oxygen dynamics assume that no microbial activity (and thus OM mineralization) occurs within the anaerobic fraction (Currie 1961; Smith 1980; Arah and Vinten 1995). The most recent C cycling models (Koven et al. 2013; Riley et al. 2011), however, use a dimensionless scaling factor (r_{oxygen}) to account for the impact of anaerobic conditions on C oxidation (or OM mineralization). It is defined as

$$r_{oxygen} = \frac{k_{min(anaerobic)}}{k_{min(aerobic)}}, \quad (1)$$

with $k_{min(anaerobic)}$ and $k_{min(aerobic)}$ as the OM mineralization rates measured during anaerobic or aerobic incubations of the same soil, respectively. This scaling factor accounts for the presumed impact of oxygen limitations in the anaerobic fraction of the soil ($f_{anaerobic}$) on the mineralization rate (k_{min}) where

$$k_{min} = k_0 r_{temperature} r_{moisture} r_{depth} r_{oxygen}, \quad (2)$$

with k_0 as the maximum rate and $r_{temperature}$, $r_{moisture}$, and r_{depth} accounting for the effects of temperature, moisture and depth on k_{min} within the anaerobic fraction. Cited values for r_{oxygen} range from 0.025 to 0.4 (Segers 1998; Frolking et al. 2001; Wania et al. 2009). These values are exclusively taken from peat cores where the reduction in oxidation rates was measured by comparing anaerobic with aerobic incubations, with a value of 0.15 for instance showing that the anaerobic C oxidation rate is 15 % of that measured under aerobic conditions. Due to the large range of reported values, an average value of 0.2 is used to represent r_{oxygen} in models (Koven et al. 2013; Riley et al. 2011). However, the large variability also suggests that r_{oxygen} strongly depends on a soil's properties, and values are expected to vary significantly for soil ecosystems other than peat. We therefore argue that r_{oxygen} is a soil-specific parameter, and is thus best estimated using soil characteristics. To our knowledge, no study has systematically assessed how the characteristics of mineral soils (as opposed to peat) impact r_{oxygen} . Since r_{oxygen} is a direct function of $k_{min,anaerobic}$, understanding factors influencing anaerobic C oxidation could provide a useful means to improved estimates of r_{oxygen} for a given soil environment. Anaerobic respiration requires microbial access to (i) C sources that can be either fermented (products of which that are then used for respiration) or directly respired and (ii) the availability of suitable alternative TEAs (Postma and Jakobsen 1996). The bioavailability

and reactivity of C substrates and TEAs such as Mn and Fe oxides may thus play a dominant role in determining respiration rates under anaerobic conditions, and by association, r_{oxygen} . Which soil characteristics (e.g., C or TEA availability) are useful as predictors of r_{oxygen} in upland soils has yet to be shown.

Metabolic constraints on anaerobic OM metabolism

Under both aerobic and anaerobic conditions microbial decomposition of OM is thought to occur in a step-wise fashion (Hedges and Keil [1995](#)). The first, and rate-limiting, step is the production of soluble and assimilable organic compounds. Under aerobic conditions, oxygen mediates the depolymerization of particulate OM (both plant and microbe-derived) into smaller fragments either through oxidative enzymes (Sinsabaugh [2010](#)) or reactive metal species (Sunda and Kieber [1994](#); Hall et al. [2014a](#)), first into smaller macromolecules and then into soluble compounds small enough (<1000 Da) to be assimilated through cell walls and metabolized inside the cell. Under anaerobic conditions, depolymerization relies primarily on hydrolytic enzymes, and fermenters compete for lower-molecular weight products (Leschine [1995](#); Postma and Jakobsen [1996](#); Megonigal et al. [2003](#)). Because hydrolysis is restricted to a more limited set of chemical bonds, depolymerization is often regarded as the rate-limiting step in OM decomposition in anaerobic environments (Reineke [2001](#); Freeman et al. [2001](#); Wu et al. [2001](#); Glissmann and Conrad [2002](#)) and is thought to result in the accumulation of hydrolysis-resistant materials such as lignin and lipids (Hedges and Keil [1995](#)). Although the importance of hydrolysis and fermentation reactions has received renewed attention (Castelle et al. [2013](#)), they remain the least well-defined step in anaerobic decomposition (Megonigal et al. [2003](#); Vavilin et al. [2008](#)).

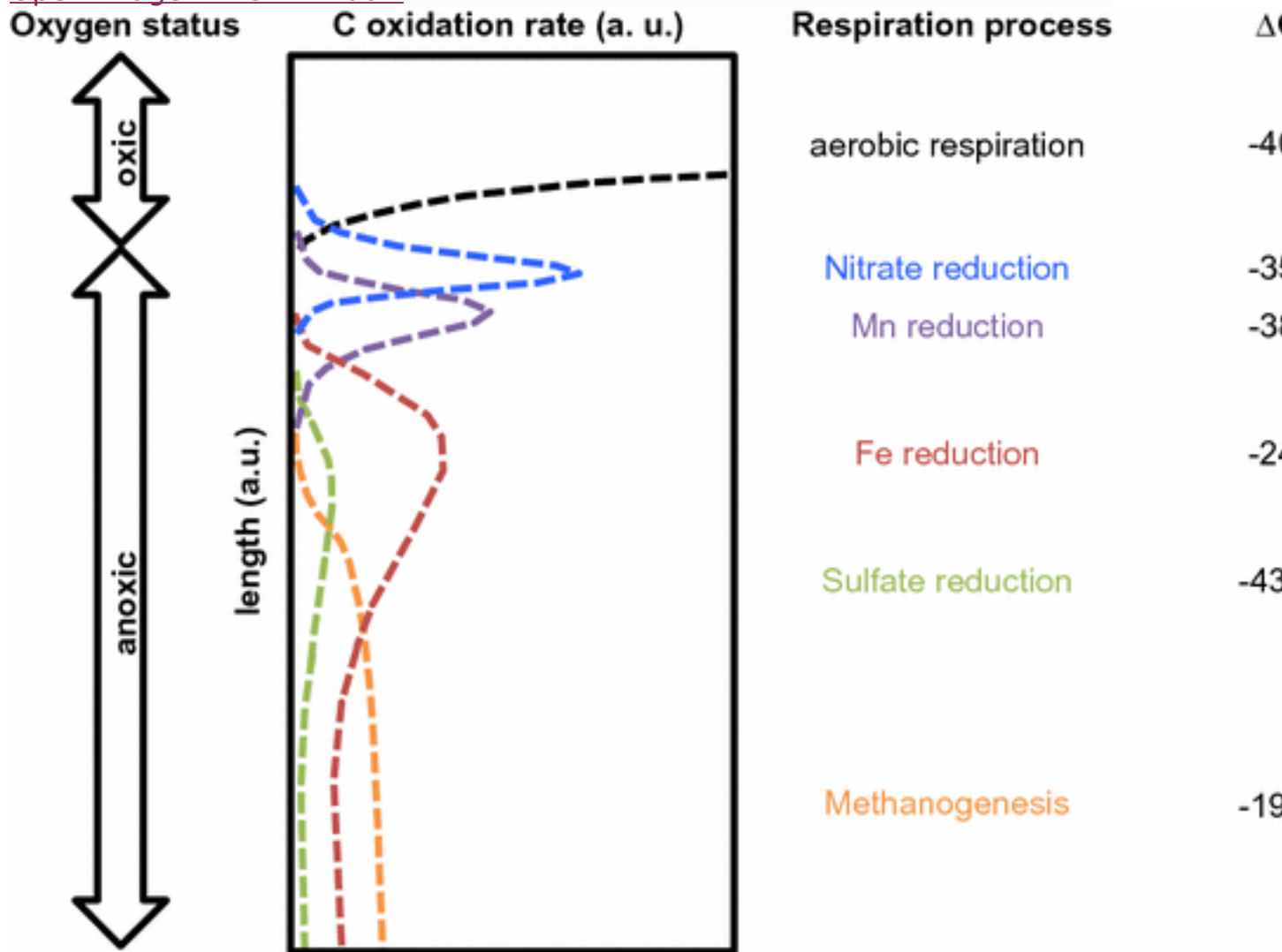
The second step in the decomposition chain is the oxidation of LMW compounds. Once assimilable LMW products generated during depolymerization and fermentation are taken up into cells, their oxidation to CO_2 can be coupled to the reduction of alternative TEAs such as NO_3^- , NO_2^- , Mn(III/IV), Fe(III), SO_4^{2-} or OM. Traditionally, anaerobic organic C oxidation has been thought of as controlled by the bioenergetic yield of the electron-accepting process (i.e., the reduction half-reaction) (Claypool and Kaplan [1974](#); Froelich et al. [1979](#); Stumm and Morgan [1996](#); Postma and Jakobsen [1996](#)). Here rates would follow in the order NO_3^- , NO_2^- , Mn(III/IV), Fe(III), SO_4^{2-} , and CO_2 which progressively decreases down the redox ladder (Arndt et al. [2013](#)) (Fig. 2). However, to fully evaluate the bioenergetics of a given redox reaction, both electron donor and acceptor half reactions have to be considered. Recently, a new formalism has been put forward that better captures the thermodynamic influence on C oxidation rates by explicitly considering the

bioenergetics of the donor half reaction and the efficiency of the electron transport chain (Jin and Bethke 2003). As derived by Jin and Bethke (2003), C oxidation rate can be expressed as:

$$\text{Rate}_{\text{C-oxidation}} = R_{\text{max}} X F_k F_T, \text{Rate}_{\text{C-oxidation}} = R_{\text{max}} X F_k F_T, \quad (3)$$

where R_{max} and X are again the maximum reaction rate and of the microbial biomass, respectively. The functions F_k and F_T are non-dimensional and vary between 0 and 1. F_k represents the microbe's ability to acquire and process reactants, thus accounting for enzyme kinetics expressed within the typical Michaelis-Menten or Monod equations; it also encompasses mineral protection and physical isolation. What has largely not been considered in microbial decomposition of OM is, F_T , the catabolic energy yield that links the rate of reaction to the thermodynamic driving force.

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*Standard Gibbs free energy with acetate as an electron donor (kJ per reaction, ΔG)

Fig. 2

Conceptualized distribution of common terminal electron accepting processes and their relative contribution to overall C oxidation across redox gradients expected in anaerobic microsites, and the Gibbs free energy yield of each electron accepting process when coupled with the oxidation of acetate

$$F_T = 1 - \exp(\Delta G_{rxn} + m\Delta G_{ATP} / nRT). F_T = 1 - \exp(\Delta G_{rxn} + m\Delta G_{ATP} / nRT). \quad (4)$$

In Eq. 4, ΔG_{rxn} is the Gibbs free energy of reaction, ΔG_{ATP} is the Gibbs free energy for ATP synthesis, n is the stoichiometry of the reaction, and m is the stoichiometry of ATP produced per formula reaction, R and T are the universal gas constant and (absolute) temperature.

The function F_T represents a fundamental bioenergetic control on microbial C oxidation and is dependent on the Gibbs free energy term ΔG_{rxn} for the overall reaction. ΔG_{rxn} is dependent on the oxidation half-reaction for the C substrate (denoted $\Delta G_{oC-ox} \Delta GC-oxo$) and the reduction half-reaction of the TEA ($\Delta G_{oTEA} \Delta GTEAo$). LaRowe and Van Cappellen (2011) recently established a general relationship that allows estimation of $\Delta G_{oC-ox} \Delta GC-oxo$ values for a given organic compound based on its nominal oxidation state of C, or NOSC ($\Delta G_{oC-ox} \Delta GC-oxo = 13.81 - 3.57 \text{ NOSC}$). The NOSC for an organic compound can be derived from the following half-reaction (Eq. 5):

$$\text{CaHbNcOdPeSzf} + (3a + 4e - d)\text{H}_2\text{O} \rightarrow a\text{HCO}_3^- + c\text{NH}_4^+ + e\text{HPO}_4^{2-} + f\text{HS}^- + (5a + b - 4c - 2d + 7e - f)\text{H}^+ + (-Z + 4a + b - 3c - 2d + 5e - 2f)e^-$$

$$\text{CaHbNcOdPeSzf} + (3a + 4e - d)\text{H}_2\text{O} \rightarrow a\text{HCO}_3^- + c\text{NH}_4^+ + e\text{HPO}_4^{2-} + f\text{HS}^- + (5a + b - 4c - 2d + 7e - f)\text{H}^+ + (-Z + 4a + b - 3c - 2d + 5e - 2f)e^- \quad (5)$$

With

$$\text{NOSC} = -((-Z + 4a + b - 3c - 2d + 5e - 2f)/a) + 4. \text{NOSC} = -((-Z + 4a + b - 3c - 2d + 5e - 2f)/a) + 4. \quad (6)$$

Here, Z corresponds to the net charge of the organic compound, and the subscripts a , b , c , d , e and f refer to the stoichiometric numbers of the elements C, H, N, O, P and S. The NOSC term can thus be used to predict $\Delta G_{oC-ox} \Delta GC-oxo$ for the oxidation of an organic compound simply through their composition (i.e., their molecular structure need not be known): this concept provides an easy means to calculate the thermodynamic driving force, F_T , for the microbial oxidation of a C compound when coupled to predominant TEAs in environmental systems (Fig. 3a). When coupled to oxygen, F_T is close to 1, and the reaction is expected to proceed almost uninhibited for compounds spanning the full range of

NOSCs. However, under anaerobic conditions when oxidation is coupled to the reduction of Fe(III)—the most important alternative electron acceptor in upland soils—a very different scenario results. F_T for reduced substrates with NOSCs of less than -1.75 is zero, i.e., microbial oxidation is thermodynamically inhibited. Only for very oxidized substrates such as simple organic acids, with generally positive NOSC values, will microbial oxidation proceed unimpeded. As Fig. 1b illustrates, microbial oxidation of abundant compound classes such as lipids (fatty acids and waxes) and lignins will not just be kinetically slower but rather thermodynamically inhibited.

[Open image in new window](#)

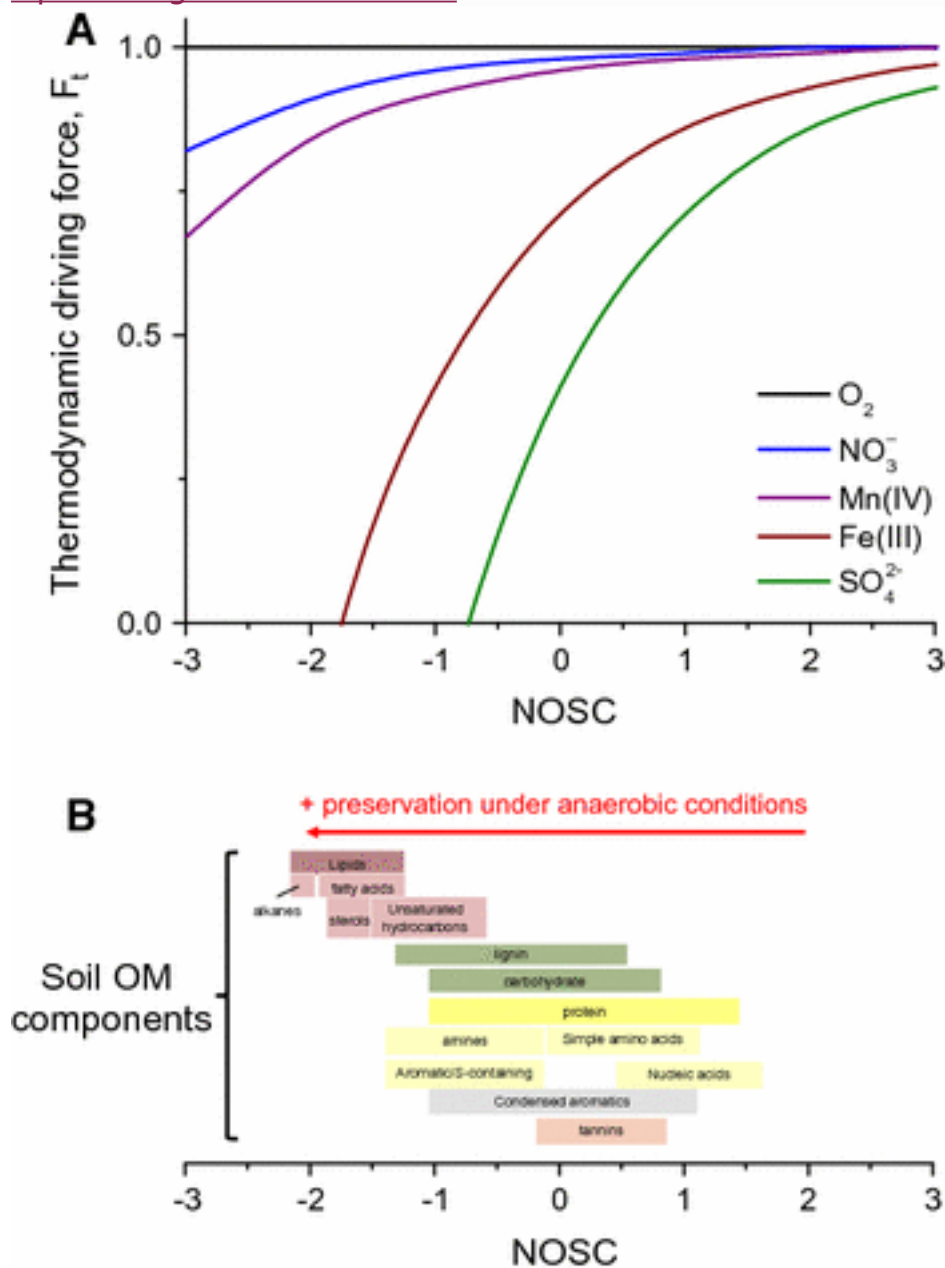


Fig. 3

a Thermodynamic driving force for the oxidation of OM as a function of nominal oxidation state of carbon (NOSC). **b** Range of NOSC values for a range of soil organic matter components. Values are estimated based on the approximate position of each compound class in Van Krevelen diagrams

Relatively long turnover times of highly reduced compound classes in upland soils provide further support for the notion that oxygen limitations impose metabolic constraints on OM mineralization. Aliphatic compounds, derived from cutin, suberin, waxes and lipids, are believed to be the most persistent components of soil OM (Baldock et al. [1992](#); Riederer et al. [1993](#); Baldock and Skjemstad [2000](#); Rumpel [2004](#); Rumpel et al. [2004](#); Mikutta et al. [2006](#); Kelleher et al. [2006](#); Lorenz et al. [2007](#); Clemente et al. [2011](#)) and accumulate in finer particle-size fractions (Baldock et al. [1992](#); Lorenz et al. [2007](#); Clemente et al. [2011](#)), in subsoils (Rumpel and Kögel-Knabner [2011](#)), and with increasing precipitation (Pisani et al. [2014](#)). More recently, Malik et al. ([2015](#)) showed that turnover of microbial lipids is significantly slower than that of microbial nucleic acids, leading the authors to conclude that these microbial compound classes contribute differently to soil C storage. The kinetics and thermodynamics of C oxidation (detailed above) suggests that metabolic constraints under anaerobic conditions preferentially preserve highly reduced compounds such as aliphatics (Fig. [3b](#)). Moreover, accumulation of aliphatic compounds in clay-rich soil environment and with increasing rainfall—both finer particle size and soil moisture restrict oxygen diffusion rates—suggests oxygen limitations impact their preservation.

Conclusions

Multiple lines of evidence converge to indicate that anaerobic microsites are not only ubiquitous in most upland soils, but also that metabolic constraints prevailing in these microenvironments have a strong effect on C oxidation rates and ultimately storage. Based on the evidence presented here, we propose that oxygen limitation is a hitherto largely underestimated mechanism restricting C oxidation in uplands soils. However, we also find that the model representation of anaerobic microsites and their impacts on overall C oxidation rates needs improvement. Contemporary modeling approaches for estimating an 'anaerobic fraction', $f_{anaerobic}$, lack experimental validation and the underlying assumptions for how $f_{anaerobic}$ affects overall rates (r_{oxygen}) are based on empirical relationships established for an ecosystem that is very different from any upland soil environment (peat). Before we can reliably quantify the impact of oxygen limitations on overall C oxidation rates in different upland soils, the following knowledge gaps have to be addressed.

First, elucidating the controls on the formation and persistence of anaerobic microsites may better constrain estimates of the anaerobic domain size

($f_{\text{anaerobic}}$) in upland soils. While the effects of soil moisture have received much attention (Linn and Doran 1984; Skopp et al. 1990; Manzoni et al. 2012; Moyano et al. 2013), the roles of soil architecture (e.g., structure and texture) and C availability in determining the balance between oxygen supply via diffusion and consumption via heterotrophic respiration are more poorly resolved. Furthermore, the involvement of roots in generating anaerobic zones (Fischer et al. 1989; Richter et al. 2007; Fimmen et al. 2008), mediated through either root respiration (Bidel et al. 2000) or the supply of fresh C (Hojberg and Sorensen 1993; Keiluweit et al. 2015), warrants further attention. Additionally, defining the roles of reactive intermediates generated at aerobic-anaerobic interfaces surrounding anaerobic microsites could provide a more nuanced view of their impact on C cycling (Roden et al. 2004; Thompson et al. 2005; Hall et al. 2014b). A better understanding of the interactions among soil architecture, C availability, and root and microbial activity in creating persistent anaerobic microsites would improve our ability to predict the extent of anaerobic pore domains in modeling frameworks.

Second, identifying the factors influencing metabolic rates in anaerobic microsites will improve predictions of r_{oxygen} for different soil environments. Anaerobic C oxidation rates likely depend on direct access to (i) organic compounds that can be metabolized by hydrolysis, fermented and/or respired by consortia of anaerobic microbes and (ii) suitable TEAs. It thus remains to be seen whether, for instance, the abundance of non-hydrolyzable OM or reducible Fe(III) hydroxides could serve as predictive parameters for anaerobic metabolic rates in upland soils.

Third, examining to what extent kinetic and thermodynamic controls on OM mineralization under anaerobic conditions (Freeman et al. 2001; Jin and Bethke 2003; LaRowe and Van Cappellen 2011) improve the prediction of residence times for organic compounds in upland soils. Circumstantial evidence presented here suggests that the preferential preservation of aliphatics observed in many upland soils may be explained by oxygen limitations, and associated thermodynamic trapping in anaerobic microsites. It is often assumed that these compounds are protected by their molecular structure, which renders them inherently recalcitrant or results in protective associations with minerals. If oxygen limitations were to be a dominant factor in the preservations of these compounds, reactive transport models of microbial C cycling in upland soils (Riley et al. 2014; Tang and Riley 2014) should incorporate thermodynamic constraints on heterotrophic respiration in addition to existing kinetic controls on depolymerization reactions. Novel approaches that integrate data on chemical transformation of organic compounds and possibly gene expression (e.g., for genes transcribing for oxidative exoenzymes or TEA processes) with reactive transport models may

be needed to quantify such metabolic constraints within anaerobic soil environments.

If the relative importance of oxygen limitations in the long-term preservation of organic compounds is greater than previously anticipated, the residence time of these compounds may be more susceptible to climate change impacts. Timing and intensity of precipitation events or drought conditions are expected to change with warmer global temperatures (Greve et al. [2014](#); Frank et al. [2015](#); Wasko and Sharma [2015](#)), with direct consequences for soil oxygen dynamics. For example, more intense but less frequent precipitation events may increase the size of anaerobic domains in soils. Conversely, prolonged droughts may increase oxygen supply into the soil. It is currently not possible to predict the persistence of anaerobic microsites and their impact on C oxidation rates under these changing conditions. Identifying the factors influencing the formation and persistence of anaerobic microsites, and their relative impact of oxygen limitations on oxidation rates of soil C, would substantially improve predictions of soil C dynamics in a changing climate.

Notes

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