Biogeochemistry (2016) 127:157–171
DOI 10.1007/s10533-015-0180-6

SYNTHESIS AND EMERGING IDEAS

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

**Marco Keiluweit · Peter S. Nico · Markus Kleber · Scott Fendorf**

Received: 18 July 2015 / Accepted: 29 December 2015 / Published online: 22 January 2016

**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) |

---

Responsible Editor: Dr. Sharon A. Billings.

M. Keiluweit · S. Fendorf (✉)
Department of Earth System Science, Stanford University,
473 Via Ortega, Stanford, CA 94305-4015, USA
e-mail: fendorf@stanford.edu

M. Keiluweit
Stockbridge School of Agriculture, University of
Massachusetts Amherst, Amherst, MA, USA

P. S. Nico
Earth Science Division, Lawrence Berkeley National
Laboratory, Berkeley, CA, USA

M. Kleber
Department of Crop and Soil Science, Oregon State
University, Corvallis, OR, USA

| | |
|---|---|
| $F_t$ | 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) |

## 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 $CO_2$) 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 laucustrian 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.

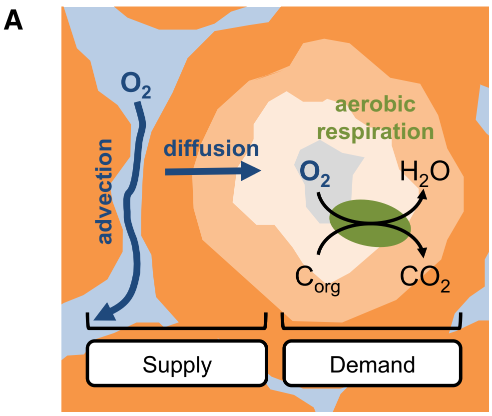
Here we seek to critically evaluate whether such oxygen limitations within upland soils contribute significantly to the preservation of OM in soils. We specifically aim to (i) document what is known about the extent of anaerobic microsites in upland soils and how they are represented in C cycling models, (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 no 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 µm), 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.



**B**

| via oxygen diffusion | |
|---|---|
| **Factor** | **Soil properties** |
| Water configuration | - water content<br>- pore water distribution<br>- water film thickness |
| Soil architecture | - pore size distribution<br>- aggregate radius<br>- particle size distribution (texture)<br>- porosity<br>- tortuosity<br>- pore connectivity<br>- soil depth (distance from atmosphere) |

| via oxygen consumption | |
|---|---|
| **Factor** | **Soil properties** |
| Microbial activity | - active microbial biomass<br>- functional capacity |
| $C_{org}$ | - C concentration<br>- accessibility (solubility, association with minerals)<br>- molecular size (polymer versus monomer)<br>- oxygen demand (stoichiometric oxygen demand for complete substrate oxidation) |
| Nutrients (e.g., N and P) | - concentration<br>- availability |

**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 $H_2/CO_2$-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 Horwáth 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., $CO_2$ 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 $CO_2$. 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

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

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

$$k_{\min} = k_0 r_{temperature} r_{moisture} r_{depth} r_{oxygen}, \tag{2}$$

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 stepwise 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 $NO_3^-$, 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 $NO_3^-$, 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:

$$\mathrm{Rate}_{\mathrm{C-oxidation}} = \mathrm{R_{max} X F_k F_T}, \tag{3}$$

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.

$$\mathrm{F_T} = 1 - \exp\left(\frac{\Delta G_{rxn} + m\Delta G_{ATP}}{nRT}\right). \tag{4}$$

In Eq. 4, $\Delta G_{rxn}$ is the Gibb's free energy of reaction, $\Delta G_{ATP}$ 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.

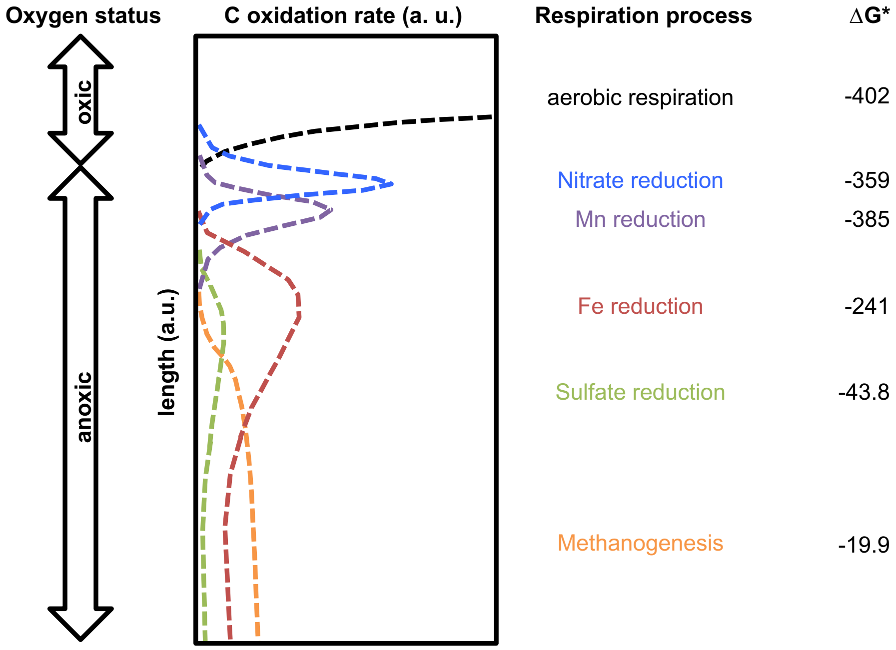
The function $F_T$ represents a fundamental bioenergetic control on microbial C oxidation and is dependent on the Gibbs free energy term $\Delta G_{rxn}$ for the overall reaction. $\Delta G_{rxn}$ is dependent on the oxidation half-reaction for the C substrate (denoted $\Delta G^o_{C-ox}$) and the reduction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

$$\begin{aligned} &C_aH_bN_cO_dP_eS_f^z + (3a + 4e - d)H_2O \\ &\quad \rightarrow aHCO_3^- + cNH_4^+ + eHPO_4^{2-} + fHS^- \\ &\quad + (5a + b - 4c - 2d + 7e - f)H^+ \\ &\quad + (-Z + 4a + b - 3c - 2d + 5e - 2f)e^-, \end{aligned} \tag{5}$$

With

$$\begin{aligned} \mathrm{NOSC} = &-((-Z + 4a + b - 3c - 2d + 5e - 2f)/a) \\ &+ 4. \end{aligned} \tag{6}$$

Here, Z corresponds to the net charge of the organic compound, and the subscripts $a$, $b$, $c$, $d$, $e$ and



*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* refer to the stoichiometric numbers of the elements C, H, N, O, P and S. The NOSC term can thus be used to predict $\Delta G^{o}_{C-ox}$ 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.

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

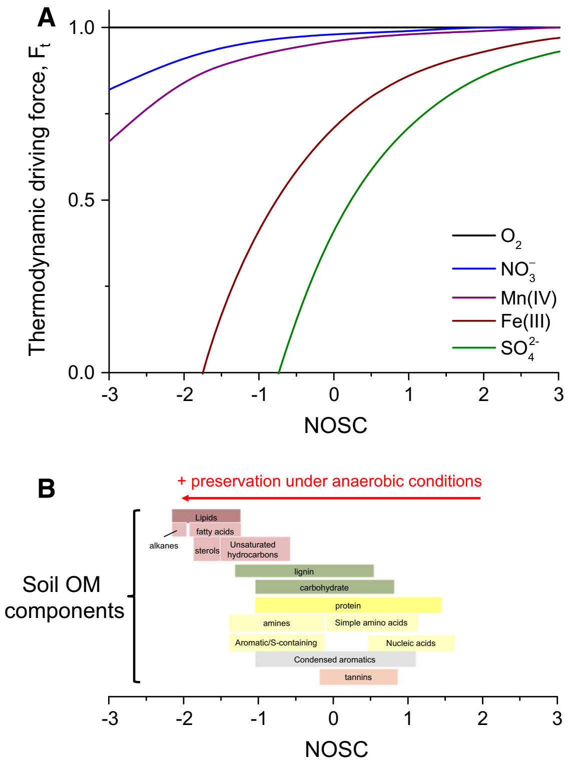


**Fig. 3** **a** Thermodynamic driving force for the oxidation of OM as a function of nominal oxidation state of carbon (NOSC). **b** Range of NOSC values for a range of soil organic matter components. Values are estimated based on the approximate position of each compound class in Van Krevelen diagrams

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 ($f_{anaerobic}$) 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.

**Acknowledgments** This work was supported by the US Department of Energy, Office of Biological and Environmental Research, Terrestrial Ecosystem Program (Award Number DE-FG02-13ER65542). We would also like to thank Patrick Megonigal and an anonymous reviewer for their help in improving this manuscript.

## References

Amelung W, Kaiser K, Kammerer G, Sauer G (2002) Organic carbon at soil particle surfaces—evidence from X-ray photoelectron spectroscopy and surface abrasion. Soil Sci Soc Am J 66:1526–1530

Andersen BL, Bidoglio G, Leip A, Rembges D (1998) A new method to study simultaneous methane oxidation and methane production in soils. Glob Biogeochem Cycles 12:587–594. doi:10.1029/98GB01975

Angel R, Claus P, Conrad R (2012) Methanogenic archaea are globally ubiquitous in aerated soils and become active under wet anoxic conditions. ISME J 6:847–862. doi:10.1038/ismej.2011.141

Arah JRM, Smith KA (1989) Steady-state denitrification in aggregated soils: a mathematical model. J Soil Sci 40:139–149. doi:10.1111/j.1365-2389.1989.tb01262.x

Arah JRM, Vinten AJA (1995) Simplified models of anoxia and denitrification in aggregated and simple-structured soils. Eur J Soil Sci 46:507–517. doi:10.1111/j.1365-2389.1995.tb01347.x

Arndt S, Jørgensen BB, LaRowe DE et al (2013) Quantifying the degradation of organic matter in marine sediments: a review and synthesis. Earth Sci Rev 123:53–86. doi:10.1016/j.earscirev.2013.02.008

Bailey VL, Bilskis CL, Fansler SJ et al (2012) Measurements of microbial community activities in individual soil macroaggregates. Soil Biol Biochem 48:192–195. doi:10.1016/j.soilbio.2012.01.004

Baldock JA, Skjemstad JO (2000) Role of the soil matrix and minerals in protecting natural organic materials against biological attack. Org Geochem 31:697–710

Baldock JA, Oades JM, Waters AG et al (1992) Aspects of the chemical structure of soil organic materials as revealed by solid-state $^{13}$C NMR spectroscopy. Biogeochemistry 16:1–42. doi:10.1007/BF02402261

Bartlett RJ (1988) Manganese redox reactions and organic interactions in soils. In: Graham RD, Hannam RJ, Uren NC (eds) Manganese in soils and plants. Springer, Dordrecht, pp 59–73

Bidel LPR, Renault P, Pagès L, Rivière LM (2000) Mapping meristem respiration of *Prunus persica* (L.) Batsch seedlings: potential respiration of the meristems, $O_2$ diffusional constraints and combined effects on root growth. J Exp Bot 51:755–768. doi:10.1093/jexbot/51.345.755

Bridge BJ, Rixon AJ (1976) Oxygen uptake and respiratory quotient of field soil cores in relation to their air-filled pore space. J Soil Sci 27:279–286

Bundt M, Jäggi M, Blaser P et al (2001a) Carbon and nitrogen dynamics in preferential flow paths and matrix of a forest soil. Soil Sci Soc Am J 65:1529–1538

Bundt M, Widmer F, Pesaro M et al (2001b) Preferential flow paths: biological "hot spots" in soils. Soil Biol Biochem 33:729–738. doi:10.1016/S0038-0717(00)00218-2

Castelle CJ, Hug LA, Wrighton KC et al (2013) Extraordinary phylogenetic diversity and metabolic versatility in aquifer sediment. Nat Commun. doi:10.1038/ncomms3120

Chacon N, Silver WL, Dubinsky EA, Cusack DF (2006) Iron reduction and soil phosphorus solubilization in humid tropical forests soils: the roles of labile carbon pools and an electron shuttle compound. Biogeochemistry 78:67–84. doi:10.1007/s10533-005-2343-3

Claypool GE, Kaplan IR (1974) The origin and distribution of methane in marine sediments. In: Kaplan IR (ed) Natural gases in marine sediments. Springer, New York, pp 99–139

Clemente JS, Simpson AJ, Simpson MJ (2011) Association of specific organic matter compounds in size fractions of soils under different environmental controls. Org Geochem 42:1169–1180. doi:10.1016/j.orggeochem.2011.08.010

Cotrufo MF, Wallenstein MD, Boot CM et al (2013) The microbial efficiency-matrix stabilization (MEMS) framework integrates plant litter decomposition with soil organic matter stabilization: do labile plant inputs form stable soil organic matter? Glob Change Biol 19:988–995. doi:10.1111/gcb.12113

Currie J (1961) Gaseous diffusion in the aeration of aggregated soils. Soil Sci 92:40–45

Currie JA (1984) Gas diffusion through soil crumbs: the effects of compaction and wetting. J Soil Sci 35:1–10. doi:10.1111/j.1365-2389.1984.tb00253.x

Davidson EA, Samanta S, Caramori SS, Savage K (2012) The dual Arrhenius and Michaelis–Menten kinetics model for decomposition of soil organic matter at hourly to seasonal time scales. Glob Change Biol 18:371–384. doi:10.1111/j.1365-2486.2011.02546.x

De Gryze S, Jassogne L, Six J et al (2006) Pore structure changes during decomposition of fresh residue: X-ray tomography analyses. Geoderma 134:82–96. doi:10.1016/j.geoderma.2005.09.002

De-Campos AB, Huang C, Johnston CT (2011) Biogeochemistry of terrestrial soils as influenced by short-term flooding. Biogeochemistry 111:239–252. doi:10.1007/s10533-011-9639-2

Devêvre OC, Horwáth WR (2000) Decomposition of rice straw and microbial carbon use efficiency under different soil temperatures and moistures. Soil Biol Biochem 32:1773–1785. doi:10.1016/S0038-0717(00)00096-1

Ewing SA, Sanderman J, Baisden WT et al (2006) Role of large-scale soil structure in organic carbon turnover: evidence from California grassland soils. J Geophys Res Biogeosci. doi:10.1029/2006JG000174

Fan Z, Neff JC, Waldrop MP et al (2014) Transport of oxygen in soil pore–water systems: implications for modeling emissions of carbon dioxide and methane from peatlands. Biogeochemistry. doi:10.1007/s10533-014-0012-0

Fiedler S, Kalbitz K (2003) Concentrations and properties of dissolved organic matter in forest soils as affected by the redox regime. Soil Sci 168:793–801

Fiedler S, Vepraskas MJ, Richardson JL (2007) Soil redox potential: importance, field measurements, and observations. In: Sparks DL (ed) Advances in agronomy. Academic, San Diego, pp 1–54

Fimmen RL Jr, de Richter DB, Vasudevan D et al (2008) Rhizogenic Fe–C redox cycling: a hypothetical biogeochemical mechanism that drives crustal weathering in upland soils. Biogeochemistry 87:127–141. doi:10.1007/s10533-007-9172-5

Fischer WR, Flessa H, Schaller G (1989) pH values and redox potentials in microsites of the rhizosphere. Z Pflanzenernaehr Bodenk 152:191–195. doi:10.1002/jpln.19891520209

Frank D, Reichstein M, Bahn M et al (2015) Effects of climate extremes on the terrestrial carbon cycle: concepts, processes and potential future impacts. Glob Change Biol. doi:10.1111/gcb.12916

Freeman C, Ostle N, Kang H (2001) An enzymic “latch” on a global carbon store. Nature 409:149–149. doi:10.1038/35051650

Froelich PN, Klinkhammer GP, Bender ML et al (1979) Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim Cosmochim Acta 43:1075–1090. doi:10.1016/0016-7037(79)90095-4

Frolking S, Roulet NT, Moore TR et al (2001) Modeling northern peatland decomposition and peat accumulation. Ecosystems 4:479–498. doi:10.1007/s10021-001-0105-1

Fuss CB, Driscoll CT, Johnson CE et al (2010) Dynamics of oxidized and reduced iron in a northern hardwood forest. Biogeochemistry 104:103–119. doi:10.1007/s10533-010-9490-x

Glissmann K, Conrad R (2002) Saccharolytic activity and its role as a limiting step in methane formation during the anaerobic degradation of rice straw in rice paddy soil. Biol Fertil Soils 35:62–67. doi:10.1007/s00374-002-0442-z

Greenwood DJ (1961) The effect of oxygen concentration on the decomposition of organic materials in soil. Plant Soil 14:360–376. doi:10.1007/BF01666294

Greve P, Orlowsky B, Mueller B et al (2014) Global assessment of trends in wetting and drying over land. Nat Geosci 7:716–721. doi:10.1038/ngeo2247

Hall SJ, McDowell WH, Silver WL (2013) When wet gets wetter: decoupling of moisture, redox biogeochemistry, and greenhouse gas fluxes in a humid tropical forest soil. Ecosystems 16:576–589. doi:10.1007/s10021-012-9631-2

Hall SJ, Treffkorn J, Silver WL (2014) Breaking the enzymatic latch: impacts of reducing conditions on hydrolytic enzyme activity in tropical forest soils. Ecology 95:2964–2973. doi:10.1890/13-2151.1

Hansel CM, Fendorf S, Jardine PM, Francis CA (2008) Changes in cacterial and archaeal community structure and functional diversity along a geochemically variable soil profile. Appl Environ Microbiol 74:1620–1633. doi:10.1128/AEM.01787-07

Hartnett HE, Keil RG, Hedges JI, Devol AH (1998) Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. Nature 391:572–575. doi:10.1038/35351

Hedges JI, Keil RG (1995) Sedimentary organic matter preservation: an assessment and speculative synthesis. Mar Chem 49:81–115. doi:10.1016/0304-4203(95)00008-F

Hojberg O, Sorensen J (1993) Microgradients of microbial oxygen consumption in a barley rhizosphere model system. Appl Environ Microbiol 59:431–437

Hong H, Gu Y, Yin K et al (2010) Red soils with white net-like veins and their climate significance in south China. Geoderma 160:197–207. doi:10.1016/j.geoderma.2010.09.019

Jacobs PM, West LT, Shaw JN (2002) Redoximorphic features as indicators of seasonal saturation, Lowndes County, Georgia. Soil Sci Soc Am J 66:315–323

Jarvis NJ (2007) A review of non-equilibrium water flow and solute transport in soil macropores: principles, controlling factors and consequences for water quality. Eur J Soil Sci 58:523–546. doi:10.1111/j.1365-2389.2007.00915.x

Jin Q, Bethke CM (2003) A new rate law describing microbial respiration. Appl Environ Microbiol 69:2340–2348. doi:10.1128/AEM.69.4.2340-2348.2003

Kane ES, Chivers MR, Turetsky MR et al (2013) Response of anaerobic carbon cycling to water table manipulation in an Alaskan rich fen. Soil Biol Biochem 58:50–60. doi:10.1016/j.soilbio.2012.10.032

Keiluweit M, Bougoure JJ, Nico PS et al (2015) Mineral protection of soil carbon counteracted by root exudates. Nat Clim Change 5:588–595. doi:10.1038/nclimate2580

Kelleher BP, Simpson MJ, Simpson AJ (2006) Assessing the fate and transformation of plant residues in the terrestrial environment using HR-MAS NMR spectroscopy. Geochim Cosmochim Acta 70:4080–4094. doi:10.1016/j.gca.2006.06.012

Killham K, Amato M, Ladd JN (1993) Effect of substrate location in soil and soil pore–water regime on carbon turnover. Soil Biol Biochem 25:57–62

Klotzbücher T, Kaiser K, Guggenberger G et al (2011) A new conceptual model for the fate of lignin in decomposing plant litter. Ecology 92:1052–1062. doi:10.1890/10-1307.1

Köchy M, Hiederer R, Freibauer A (2015) Global distribution of soil organic carbon—Part 1: masses and frequency distributions of SOC stocks for the tropics, permafrost regions, wetlands, and the world. SOIL 1:351–365. doi:10.5194/soil-1-351-2015

Koven CD, Riley WJ, Subin ZM et al (2013) The effect of vertically resolved soil biogeochemistry and alternate soil C and N models on C dynamics of CLM4. Biogeosciences 10:7109–7131. doi:10.5194/bg-10-7109-2013

LaRowe DE, Van Cappellen P (2011) Degradation of natural organic matter: a thermodynamic analysis. Geochim Cosmochim Acta 75:2030–2042. doi:10.1016/j.gca.2011.01.020

Lee CG, Watanabe T, Murase J et al (2012) Growth of methanogens in an oxic soil microcosm: elucidation by a DNA-SIP experiment using $^{13}$C-labeled dried rice callus. Appl Soil Ecol 58:37–44. doi:10.1016/j.apsoil.2012.03.002

Leschine SB (1995) Anaerobic cellulose degradation. Annu Rev Microbiol 49:399–426

Linn DM, Doran JW (1984) Effect of water-filled pore space on carbon dioxide and nitrous oxide production in tilled and nontilled soils. Soil Sci Soc Am J 48:1267. doi:10.2136/sssaj1984.03615995004800060013x

Liptzin D, Silver WL, Detto M (2010) Temporal dynamics in soil oxygen and greenhouse gases in two humid tropical forests. Ecosystems 14:171–182. doi:10.1007/s10021-010-9402-x

Lorenz K, Lal R, Preston CM, Nierop KGJ (2007) Strengthening the soil organic carbon pool by increasing contributions from recalcitrant aliphatic bio(macro)molecules. Geoderma 142:1–10. doi:10.1016/j.geoderma.2007.07.013

Malik AA, Dannert H, Griffiths RI et al (2015) Rhizosphere bacterial carbon turnover is higher in nucleic acids than membrane lipids: implications for understanding soil carbon cycling. Front Microbiol. doi:10.3389/fmicb.2015.00268

Mangalassery S, Sjögersten S, Sparkes DL et al (2013) The effect of soil aggregate size on pore structure and its consequence on emission of greenhouse gases. Soil Tillage Res 132:39–46. doi:10.1016/j.still.2013.05.003

Manzoni S, Schimel JP, Porporato A (2012) Responses of soil microbial communities to water stress: results from a meta-analysis. Ecology 93:930–938

Mateos MP, Carcedo SG (1985) Effect of fractionation on location of enzyme activities in soil structural units. Biol Fertil Soils 1:153–159. doi:10.1007/BF00301783

Megonigal JP, Hines ME, Visscher PT (2003) Anaerobic metabolism: linkages to trace gases and aerobic processes. In: Holland HD, Turekian KK (eds) Treatise on geochemistry. Pergamon, Oxford, pp 317–424

Mikutta R, Kleber M, Torn MS, Jahn R (2006) Stabilization of soil organic matter: association with minerals or chemical recalcitrance? Biogeochemistry 77:25–56. doi:10.1007/s10533-005-0712-6

Miller AJ, Schuur EAG, Chadwick OA (2001) Redox control of phosphorus pools in Hawaiian montane forest soils. Geoderma 102:219–237. doi:10.1016/S0016-7061(01)00016-7

Moyano FE, Manzoni S, Chenu C (2013) Responses of soil heterotrophic respiration to moisture availability: an exploration of processes and models. Soil Biol Biochem 59:72–85. doi:10.1016/j.soilbio.2013.01.002

Myrold DD, Tiedje JM (1985) Diffusional constraints on denitrification in soil. Soil Sci Soc Am J 49:651–657

Navarro-García F, Casermeiro MÁ, Schimel JP (2012) When structure means conservation: effect of aggregate structure in controlling microbial responses to rewetting events. Soil Biol Biochem 44:1–8. doi:10.1016/j.soilbio.2011.09.019

Nielson KK, Rogers VC, Gee GW (1984) Diffusion of radon through soils: a pore distribution model1. Soil Sci Soc Am J 48:482. doi:10.2136/sssaj1984.03615995004800030002x

Oades JM (1988) The retention of organic matter in soils. Biogeochemistry 5:35–70. doi:10.1007/BF02180317

Parr JF, Reuszer HW (1962) Organic matter decomposition as influenced by oxygen level and flow rate of gases in the constant aeration method1. Soil Sci Soc Am J 26:552. doi:10.2136/sssaj1962.03615995002600060012x

Peters V, Conrad R (1995) Methanogenic and other strictly anaerobic bacteria in desert soil and other oxic soils. Appl Environ Microbiol 61:1673–1676

Pisani O, Hills KM, Courtier-Murias D et al (2014) Accumulation of aliphatic compounds in soil with increasing mean annual temperature. Org Geochem 76:118–127. doi:10.1016/j.orggeochem.2014.07.009

Poplawski AB, Mårtensson L, Wartiainen I, Rasmussen U (2007) Archaeal diversity and community structure in a Swedish barley field: specificity of the EK510R/(EURY498) 16S rDNA primer. J Microbiol Methods 69:161–173. doi:10.1016/j.mimet.2006.12.018

Postma D, Jakobsen R (1996) Redox zonation: equilibrium constraints on the Fe(III)/$SO_4$–reduction interface. Geochim Cosmochim Acta 60:3169–3175. doi:10.1016/0016-7037(96)00156-1

Reddy KR, Patrick WH Jr (1975) Effect of alternate aerobic and anaerobic conditions on redox potential, organic matter decomposition and nitrogen loss in a flooded soil. Soil Biol Biochem 7:87–94. doi:10.1016/0038-0717(75)90004-8

Reddy KR, D'Angelo EM, Harris WG (2000) Biogeochemistry of wetlands. In: Sumner ME (ed) Handbook of soil science. CRC Press, Boca Raton, pp G89–G119

Reineke W (2001) Aerobic and anaerobic biodegradation potentials of microorganisms. In: Beek B (ed) Biodegradation and persistance. Springer, Berlin, pp 1–161

Richter DD, Oh N-H, Fimmen R, Jackson J (2007) The rhizosphere and soil formation. The rhizosphere: an ecological perspective. Academic, Amsterdam, pp 179–200

Riederer M, Matzke K, Ziegler F, Kögel-Knabner I (1993) Occurrence, distribution and fate of the lipid plant biopolymers cutin and suberin in temperate forest soils. Org Geochem 20:1063–1076. doi:10.1016/0146-6380(93)90114-Q

Rijtema PE, Kroes JG (1991) Some results of nitrogen simulations with the model ANIMO. Fertil Res 27:189–198. doi:10.1007/BF01051127

Riley WJ, Subin ZM, Lawrence DM et al (2011) Barriers to predicting changes in global terrestrial methane fluxes: analyses using CLM4Me, a methane biogeochemistry model integrated in CESM. Biogeosciences 8:1925–1953. doi:10.5194/bg-8-1925-2011

Riley WJ, Maggi FM, Kleber M et al (2014) Long residence times of rapidly decomposable soil organic matter: application of a multi-phase, multi-component, and vertically-resolved model (TOUGHREACTv1) to soil carbon dynamics. Geosci Model Dev Discuss 7:815–870. doi:10.5194/gmdd-7-815-2014

Roden EE, Sobolev D, Glazer B, Luther GW (2004) Potential for microscale bacterial fe redox cycling at the aerobic–anaerobic interface. Geomicrobiol J 21:379–391. doi:10.1080/01490450490485872

Rumpel C (2004) Location and chemical composition of stabilized organic carbon in topsoil and subsoil horizons of two acid forest soils. Soil Biol Biochem 36:177–190. doi:10.1016/j.soilbio.2003.09.005

Rumpel C, Kögel-Knabner I (2011) Deep soil organic matter—a key but poorly understood component of terrestrial C cycle. Plant Soil 338:143–158. doi:10.1007/s11104-010-0391-5

Rumpel C, Seraphin A, Goebel M-O et al (2004) Alkyl C and hydrophobicity in B and C horizons of an acid forest soil. J Plant Nutr Soil Sci 167:685–692. doi:10.1002/jpln.200421484

Schmidt MWI, Torn MS, Abiven S et al (2011) Persistence of soil organic matter as an ecosystem property. Nature 478:49–56. doi:10.1038/nature10386

Schuur EA, Matson PA (2001) Net primary productivity and nutrient cycling across a mesic to wet precipitation gradient in Hawaiian montane forest. Oecologia 128:431–442. doi:10.1007/s004420100671

Segers R (1998) Methane production and methane consumption: a review of processes underlying wetland methane fluxes. Biogeochemistry 41:23–51. doi:10.1023/A:1005929032764

Sexstone AJ, Revsbech NP, Parkin TB, Tiedje JM (1985) Direct measurement of oxygen profiles and denitrification rates in soil aggregates1. Soil Sci Soc Am J 49:645. doi:10.2136/sssaj1985.03615995004900030024x

Silver WL, Lugo AE, Keller M (1999) Soil oxygen availability and biogeochemistry along rainfall and topographic gradients in upland wet tropical forest soils. Biogeochemistry 44:301–328. doi:10.1007/BF00996995

Sinsabaugh RL (2010) Phenol oxidase, peroxidase and organic matter dynamics of soil. Soil Biol Biochem 42:391–404. doi:10.1016/j.soilbio.2009.10.014

Skopp J, Jawson MD, Doran JW (1990) Steady-state aerobic microbial activity as a function of soil water content. Soil Sci Soc Am J 54:1619. doi:10.2136/sssaj1990.03615995005400060018x

Smith KA (1977) Soil aeration. Soil Sci 123:284–291

Smith KA (1980) A model of the extent of anaerobic zones in aggregated soils, and its potential application to estimates of denitrification1. J Soil Sci 31:263–277. doi:10.1111/j.1365-2389.1980.tb02080.x

Smith AP, Marín-Spiotta E, de Graaff MA, Balser TC (2014) Microbial community structure varies across soil organic matter aggregate pools during tropical land cover change. Soil Biol Biochem 77:292–303. doi:10.1016/j.soilbio.2014.05.030

Stumm W, Morgan JJ (1996) Aquatic chemistry: chemical equilibria and rates in natural waters. Wiley, New York

Sunda WG, Kieber DJ (1994) Oxidation of humic substances by manganese oxides yields low-molecular-weight organic substrates. Nature 367:62–64. doi:10.1038/367062a0

Tang J, Riley WJ (2014) Weaker soil carbon-climate feedbacks resulting from microbial and abiotic interactions. Nat Clim Change. doi:10.1038/nclimate2438

Teh YA, Silver WL, Conrad ME (2005) Oxygen effects on methane production and oxidation in humid tropical forest soils. Glob Change Biol 11:1283–1297. doi:10.1111/j.1365-2486.2005.00983.x

Thompson IA, Huber DM, Guest CA, Schulze DG (2005) Fungal manganese oxidation in a reduced soil. Environ Microbiol 7:1480–1487. doi:10.1111/j.1462-2920.2005.00842.x

Thompson A, Rancourt DG, Chadwick OA, Chorover J (2011) Iron solid-phase differentiation along a redox gradient in basaltic soils. Geochim Cosmochim Acta 75:119–133. doi:10.1016/j.gca.2010.10.005

Torn MS, Trumbore SE, Chadwick OA et al (1997) Mineral control of soil organic carbon storage and turnover. Nature 389:170–173. doi:10.1038/38260

Torn MS, Vitousek PM, Trumbore SE (2005) The influence of nutrient availability on soil organic matter turnover estimated by incubations and radiocarbon modeling. Ecosystems 8:352–372. doi:10.1007/s10021-004-0259-8

van der Lee GEM, de Winder B, Bouten W, Tietema A (1999) Anoxic microsites in Douglas fir litter. Soil Biol Biochem 31:1295–1301. doi:10.1016/S0038-0717(99)00048-6

Vavilin VA, Fernandez B, Palatsi J, Flotats X (2008) Hydrolysis kinetics in anaerobic degradation of particulate organic material: an overview. Waste Manag 28:939–951. doi:10.1016/j.wasman.2007.03.028

Veen JAV, Kuikman PJ (1990) Soil structural aspects of decomposition of organic matter by micro-organisms. Biogeochemistry 11:213–233. doi:10.1007/BF00004497

Vermes J-F, Myrold DD (1992) Denitrification in forest soils of Oregon. Can J For Res 22:504–512. doi:10.1139/x92-066

von Fischer JC, Hedin LO (2002) Separating methane production and consumption with a field-based isotope pool dilution technique: methane isotope pool dilution. Glob Biogeochem Cycles 16:8-1–8-13. doi:10.1029/2001GB001448

Wania R, Ross I, Prentice IC (2009) Integrating peatlands and permafrost into a dynamic global vegetation model: 2. Evaluation and sensitivity of vegetation and carbon cycle processes. Glob Biogeochem Cycles 23:GB3015. doi:10.1029/2008GB003413

Wasko C, Sharma A (2015) Steeper temporal distribution of rain intensity at higher temperatures within Australian storms. Nat Geosci. doi:10.1038/ngeo2456

West AE, Schmidt SK (2002) Endogenous methanogenesis stimulates oxidation of atmospheric $CH_4$ in alpine tundra soil. Microb Ecol 43:408–415. doi:10.1007/s00248-001-1049-x

Wu X-L, Chin K-J, Stubner S, Conrad R (2001) Functional patterns and temperature response of cellulose-fermenting microbial cultures containing different methanogenic communities. Appl Microbiol Biotechnol 56:212–219. doi:10.1007/s002530100622

Zausig J, Stepniewski W, Horn R (1993) Oxygen concentration and redox potential gradients in unsaturated model soil aggregates. Soil Sci Soc Am J 57:908. doi:10.2136/sssaj1993.03615995005700040005x