Modeling coupled enzymatic and solute transport controls on decomposition in drying soils

S. Manzoni [a, b, *], F. Moyano [c], T. Kätterer [d], J. Schimel [e]

[a] Department of Physical Geography, Stockholm University, Svante Arrhenius väg 8C, Frescati, SE-106 91 Stockholm, Sweden
[b] Bolin Centre for Climate Research, Stockholm University, Stockholm, Sweden
[c] Department of Bioclimatology, Georg-August-Universität, Göttingen, Niedersachsen, Germany
[d] Department of Ecology, Swedish University of Agricultural Sciences, Uppsala, Sweden
[e] Department of Ecology, Evolution and Marine Biology, University of California Santa Barbara, Santa Barbara, CA, USA

ABSTRACT

Mechanistic descriptions of microbial processes are difficult to embed in ecosystem models because they require complex mathematical formulations. The interactions between microbes, soil carbon (C), and water availability are particularly complex, as they involve coupled physical (advection and diffusion in unsaturated media) and biochemical processes (enzymatic reactions, C uptake by microbes). Here we propose an approximated equation based on a quasi-equilibrium assumption that describes microbial uptake of soil C as a function of soil moisture and organic matter content during soil drying. The equation predicts that uptake depends on two terms, one dependent on soil organic C concentration and enzyme availability (analogous to a Michaelis–Menten equation) and one dependent on soil moisture via its effects on enzyme and solute mass transfer, and microbial uptake kinetics. Assuming that uptake is proportional to microbial respiration, model results are compared to measured respiration–water potential curves. Using independently estimated parameter values (except for the calibrated microbial uptake efficiency), the theoretical model captures well the respiration decline during drying and provides an explanation of respiration pulses at rewetting. Thus, this simple formulation could be employed in ecosystem models as an alternative to empirical respiration–moisture response functions.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Recent soil biogeochemical models employ nonlinear kinetic equations to describe carbon (C) mineralization, accounting for the feedback between microbial biomass, which produces extra-cellular enzymes, and soil organic matter, which is decomposed to soluble compounds by such enzymes (Schimel and Weintraub, 2003; Allison et al., 2010; Sinsabaugh and Shah, 2012; Todd-Brown et al., 2012). In these equations, however, soil moisture effects are included *a posteriori* through rate modifiers, thus neglecting possible interactions between reaction and transport processes. Understanding and capturing these interactions is a key step towards predicting biogeochemical responses to hydro-climatic changes. Interactions arise because extracellular enzymes

must first reach the complex organic compounds and then react and degrade these compounds. Enzymes and substrates in unsaturated soil may move via diffusion or mass flow, with molecular diffusion becoming the dominant mode of transport as soils dry (Jury et al., 1983) and at the smallest spatial scales (Fig. 1). Accordingly, for microbes to decompose a complex substrate three steps are required before uptake and metabolism can occur: i) transport of enzymes to the site of decomposition, ii) enzyme-mediated reaction, and iii) transport of products back to the cells (Vetter et al., 1998).

When diffusion dominates, the transport of enzymes and soluble substrate between microbial cells and organic matter compounds can be described by Fick's law as the product of diffusivity and the concentration gradient. Diffusion is limited by the amount of water-filled pores, resulting in a power-law relationship between solute diffusivity and volumetric soil moisture (Moldrup et al., 2001; Hamamoto et al., 2010). Hence, soil moisture mediates steps i) and iii) of the decomposition process, in addition to imposing physiological stress on decomposing microbes (Harris,
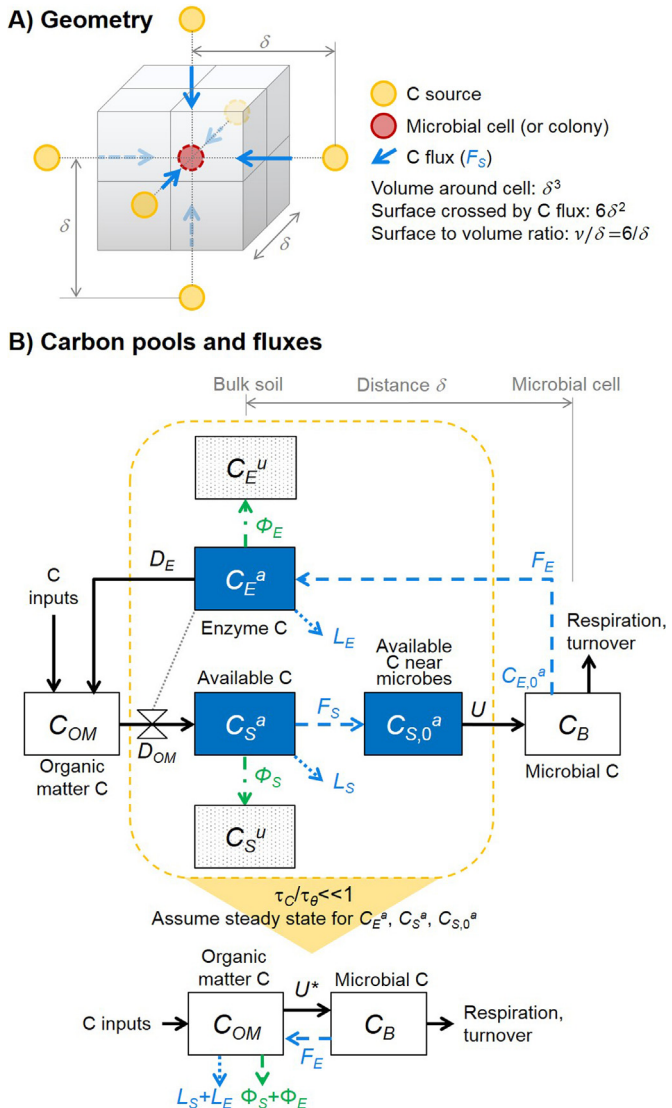
Fig. 1. A) Geometry of the substrate—microbe system. B) Illustration of the modeled C-cycle processes: diffusion (dashed blue arrows), leaching (dotted blue arrows), reaction (solid black arrows), and mass transfer to unavailable pools (dot-dashed green arrows). When transport and reaction time scales (τ_C) are shorter than organic matter (C_{OM}), microbial (C_B), and soil moisture (θ) time scales, an 'effective' steady state model for the rate of C uptake by microbes (U^*) can be obtained as a function of C_{OM}, C_B and θ (bottom scheme). The orange dashed outline includes processes that are lumped into the effective kinetic parameters at the daily time scale. Superscripts a and u respectively indicate bio-available and unavailable pools; complete symbol definitions are reported in Table 1. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

1981; Schimel et al., 2007; Manzoni et al., 2014). Natural soils, however, are highly heterogeneous, and the occurrence of 'immobile zones' may hinder Fickian diffusion by trapping solutes as they are transported towards the microbes. While the concept of immobile zones has been employed in groundwater and vadose zone solute transport models (Griffioen et al., 1998; Padilla et al., 1999; Kätterer et al., 2001; Toride et al., 2003), only recently it has been applied in the context of soil biogeochemical models (Zhang et al., 2014). Moreover, as solute concentration in the liquid phase increases in dry soils, adsorption is favored compared to desorption, and bioavailable C may be removed from the soil solution. These transport processes and physical protection mechanisms limit the availability of enzymes at the decomposition site

and of the soluble substrates that can be taken up by microbes, thus constraining the overall rate at which organic matter is transformed into new biomass.

In contrast to the transport processes, enzyme-mediated reactions (step ii) are weakly dependent on soil moisture, but they are controlled by the availability of substrates and enzymes. The rate of enzymatic reactions can be described by Michaelis—Menten kinetics, in which reaction rates saturate at high substrate concentration (Michaelis and Menten, 1913; Briggs and Haldane, 1925; Tang and Riley, 2013). The same functional dependence is often used in soil C models, on the ground that the complex, enzyme-catalyzed reactions in soils can be approximated by homogeneous reactions (Schimel and Weintraub, 2003; Davidson et al., 2012; Tang and Riley, 2013; Wang and Post, 2013; Zhang et al., 2014). The original Michaelis—Menten formalism, however, neglects the transport constraints imposed by soil moisture and no equation currently accounts for enzyme and substrate transport as well as reaction constraints in a consistent way, leaving soil moisture effects as empirical rate or C availability modifiers (Bauer et al., 2008; Davidson et al., 2012).

Macroscopic equations describing decomposition in a mechanistic way should account for these processes, albeit in a simplified way so that they can be applied in ecosystem models. The goal of this contribution is to develop an equation linking C uptake by microbes and subsequent respiration to substrate availability and soil moisture, while also accounting for enzymatic reactions and transport limitations at the daily time scale typical of most biogeochemical models. Our aim is to derive an expression where the overall effect of soil moisture on microbial respiration is not imposed *a posteriori*, but emerges from the coupling of reaction and transport processes.

2. Theory

2.1. Model rationale and main assumptions

We propose a theoretical model of carbon cycling during soil drying. As shown in Fig. 1, several conceptual C pools are considered based on their biogeochemical properties and spatial location. C pools located in the bulk soil and pools near the microbial cells are distinguished to provide a simplified, lumped description of the spatial organization in the soil micro-environment. We further separate bio-available C pools in the soil solution from pools of C trapped in hydraulically-disconnected soil patches or sorbed. A sequence of physical and reaction processes linking these pools is considered: enzyme production and transport to the reaction site, reactions yielding bio-available C and consuming stable organic matter, transport of C to the microbial cells and uptake, and removal of bioavailable C due to trapping in the un-available pools. Moreover, we focus on C pools that are degraded by extracellular enzymes and neglect labile compounds that become bioavailable as soon as they are incorporated in the soil.

In principle, a model based on mass balance equations could track the fate of C in all these pools and thus predict C fluxes among them, providing a process-based representation of C cycling in variably saturated conditions. However, most ecosystem-scale biogeochemical models lack this level of detail in their pool structure and thus require kinetic laws that account for detailed processes and yet only depend on a few modeled pools (i.e., 'macroscopic' kinetic laws). Our main goal here is to derive a 'macroscopic' kinetic law describing the flux of C from an organic matter pool to a microbial pool. We aim at collapsing the complexity illustrated in Fig. 1B (top C flow scheme) into a simple expression that only depends on pools compatible with ecosystem models (Fig. 1B, bottom). To derive this equation, we adopt the