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## Mineral properties, microbes, transport, and plant-input profiles control vertical distribution and age of soil carbon stocks



<sup>a</sup> Earth and Environmental Sciences Area, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720, United States <sup>b</sup> School of Civil Engineering, The University of Sydney, Sydney, 2006, NSW, Australia

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#### ABSTRACT

The role of organo-mineral interactions, microbial dynamics, and vertical plant input profiles are hypothesized to be important in controlling soil organic matter (SOM) stocks and dynamics. To test this hypothesis, we enhanced and applied a model (Biotic and Abiotic Model of SOM – BAMS1) that represents microbial dynamics and organo-mineral interactions integrated with a multiphase reactive transport solver for variably saturated porous media. The model represents aqueous chemistry, aqueous advection and diffusion, gaseous diffusion, sorption processes, bacterial and fungal activity, and archetypal monomer- and polymer-carbon substrate groups, including dead cell wall material. This model structure is fundamentally different, and produces different SOM dynamics, than the pseudo-first order relationships that are used in most site- and global-scale terrestrial SOM models. We simulated two grasslands, a seven-site chronosequence (~3.9-240 Ky) in Northern California, and a Russian Chernozem site where soils were sampled 100 years apart. We calibrated the model's vertically-resolved soil bulk specific surface area (SBSSA) using observed bulk SOM content, and then tested the model against observed  $\Delta^{14}$ C profiles. The modeled microbial processes, organo-mineral interactions, and vertical aqueous transport produced realistic vertically-resolved predictions of bulk SOM content,  $\Delta^{14}$ C values of SOM, lignin content, and fungi-to-aerobic bacteria biomass ratios. Using sensitivity analyses, we found that vertical carbon input profiles were important controls over the  $\Delta^{14}$ C depth distribution. Shallower carbon input profiles lead to older carbon at depth. In addition, the SBSSA was the dominant control over the magnitude and vertical distribution of SOM stocks. The findings of this study demonstrate the value of explicitly incorporating microbial activity, sorption, and vertical transport into land models to predict SOM dynamics.

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### 1. Introduction

Global soil carbon stocks are approximately three times as large as the carbon stocks in either the atmosphere or terrestrial vegetation (Schmidt et al., 2011). This carbon may be vulnerable to decomposition and release to the atmosphere due to environmental changes (e.g., thermokarst, warming). Predicting long-term changes in soil carbon storage and feedbacks with climate change requires understanding how soil organic matter (SOM) dynamics vary vertically within the soil column (Schmidt et al., 2011; Koven et al., 2013; Riley et al., 2014).

Mineral surfaces interact chemically with dissolved organic carbon (DOC) and help stabilize soil organic carbon (SOC) (Greenland, 1971; Jagadamma et al., 2012; Lutzow et al., 2006; Sibanda and Young, 1986; Sollins et al., 1996; Trumbore, 1997). The proportion and persistence of organic compounds that are at least partially protected against decomposition on soil mineral surfaces depends on several factors, including the chemical composition of the substrate, texture, mineralogy, pH, temperature, soil aggregates, and hydrologic transport (Conant et al., 2011; Gjettermann et al., 2008; Jardine et al., 1989, 1990; Kalbitz et al., 2003; Kothawala and Moore, 2009; Moore and Turunen, 2004; Six et al., 2004). Organo-mineral interactions may be especially important below the active root zone (Ahrens et al., 2015; Kalbitz et al., 2000, 2003; Masiello et al., 2004; Sanderman et al., 2008; Torn et al., 1997a) and in deeper horizons with iron, aluminum, and clay-rich minerals (Jardine et al., 1989, 1990, 2006; Kothawala







<sup>\*</sup> Corresponding author. Earth and Environmental Sciences Area, Lawrence Berkeley National Laboratory, Berkeley, CA, 94720-0001, United States. *E-mail address:* DDwivedi@lbl.gov (D. Dwivedi).

et al., 2009). These findings may partially explain the observed wide range of SOM residence times among sites, but it is presumable that interactions with mineral surfaces introduce more complexity than currently represented in terrestrial carbon cycle models.

Most land models apply a pseudo-first-order representation for soil organic matter (SOM) dynamics, with several SOM 'pools' with explicit turnover times that are dynamically affected by temperature and moisture (e.g., Century (Parton et al., 1987, 2010), RothC (Jenkinson and Coleman, 2008)). Some of these models also represent the role of mineral protection by modifying the proportional transfers between pools and the explicit turnover times as a function of mineralogy, usually clay content (Jenkinson and Coleman, 2008; Parton et al., 2010). To our knowledge, organomineral interactions are represented explicitly in only one global land model (Sulman et al., 2014). Sulman et al. (2014) argued that organo-mineral interactions help explain SOM responses in Free-Air CO<sub>2</sub> Enrichment (FACE) experiments and have global implications for future terrestrial carbon stocks. Recently, Ahrens et al. (2015) used a site-scale model (COMISSION) and observations from a site in Bavaria to demonstrate that SOC persistence is controlled by mineral surface stabilization and cyclic microbial assimilation and release. Our previous work with the BAMS1 model (Biotic and Abiotic Model of SOM; (Riley et al., 2014)) had similar conclusions. However, these models apply different approaches for sorption: Riley et al. (2014) applied separate adsorption and desorption rates to represent mineral-protected carbon, Sulman et al. (2014) described protected carbon with a first order turnover rate, and Ahrens et al. (2015) used a Langmuir sorption approach.

The level of model complexity required to accurately predict SOC dynamics under a changing climate remains unsettled (e.g., Allison et al., 2010; Luo et al., 2015; Parton et al., 2010). Riley et al. (2014) showed that representing modest microbial diversity, organic chemistry, and a reasonable combination of sorption parameters led to good matches with observed soil organic carbon profiles without resorting to an arbitrary depth-dependent decline in SOM turnover rates, as is often done in existing SOM models. Upon this premise, exploring this modeling philosophy may lead to valuable characterization of vertically-resolved soil organic matter, transport, mineral surface interaction, and microbial ecological interactions. In this work, we applied BAMS1, which includes a microbially mediated SOM reaction network with two microbial functional groups (heterotrophic aerobic bacteria and fungi) and several polymer and monomer species. Dynamic adsorption and desorption with a surface complexation model were added to the model for this work.

The specific objectives of this study are to (1) explore and quantify how bulk mineral properties affect carbon stocks and residence times of soil organic matter and (2) identify dominant controls for carbon stocks and inventory. We used sensitivity analyses and comparisons with published data to investigate controls on soil carbon stocks and turnover across a seven-site marineterrace grassland chronosequence in California (Masiello et al., 2004) and in a Chernozem steppe grassland site in Russia (Torn et al., 2002).

#### 2. Methodology and model inputs

#### 2.1. Chronosequence terrace sites in Northern California

This chronosequence comprises seven terraces on the northern California coast (between  $38^{\circ}$  to  $42^{\circ}$  N and  $122^{\circ}$  to  $125^{\circ}$  W) that were formed on the same type of beach deposits but have soil development ages of 3.9, 29, 40, 118, 124, 124, and 240 ky, leading to

significant differences in texture and mineralogical composition. We identify the Chronosequence Terrace (CT) sites as: CT-3.9ky, CT-29ky, CT-40ky, CT-118ky, CT-124ky-1, CT-124ky-2, and CT-240ky. Soil class ranges from mixed sandy soil (CT-3.9ky) to coarse loamy (CT-29ky) to fine loamy (CT-40ky to CT-240ky) along the chronosequence. Clay content increases in CT sites with the age: for example, soils on CT-3.9ky and CT-29ky have 5% and 15% maximum clav content, respectively. Soils on CT-40ky, CT-118ky, CT-124ky-1. CT-124ky-2, and CT-240ky have at least 25-30% maximum clay content (Merritts et al., 1991). Soils at the CT sites have been classified on the taxonomic soil order as Alfisols (Chadwick et al., 1990). The sites have a cool Mediterranean climate, with mean annual air temperature of 12 °C and mean annual precipitation of 1000 mm (Masiello et al., 2004; Merritts et al., 1991). These chronosequence terraces can be used to compare the effect of soil mineralogy and development while holding climate, vegetation, and other soilforming factors relatively constant.

Merritts et al. (1991) described the soil development and mineralogy of these terraces in detail. The older sites are clay-rich and contain crystalline forms of iron-rich minerals. Total SOM content and SOM radiocarbon ( $\Delta^{14}$ C) were measured in one soil profile in each of the seven terraces (Masiello et al., 2004). Measured bulk SOM content is the lowest in the CT-3.9ky site, intermediate in the CT-29ky and CT-40ky sites, and highest in the older sites (CT-118ky, CT-124ky-1, CT-124ky-2, and CT-240ky) (Masiello et al., 2004). Because the older sites have experienced more weathering and have higher clay content as compared to younger sites, they present more mineral surface area available to sorb organic carbon (Mayer, 1994).

### 2.2. Modern and 100-year-old-soil archives in Russian steppe sites

The Russian steppe soils are classified as Mollisols on the taxonomic soil order and have relatively large carbon stocks. The soil on these sites are characterized as clay-loam and granular to subgranular structure along the depth; clay content ranges from 24% to 30% in these sites (Torn et al., 2002). Several studies have been conducted in this region to better understand soil carbon stocks and turnover (Guenet et al., 2013; Torn et al., 2002). We used data from the Kammenaya Steppe Preserve (51° 02′ N, 40° 43′ E). The vegetation was typical steppe prairie, dominated by herbaceous perennials with some woody perennials. The sampling sites have a mean annual temperature of 6.4 °C and mean annual precipitation of 520 mm, with approximately 25% as snow. The snow cover typically lasts for slightly more than three months. SOM content and  $\Delta^{14}$ C values were measured in three soil profiles (Archive, Pit1, and Pit2 soils) at this site. SOM content decreases from about 8% near the surface to less than 1% at 1.5 m depth.

#### 2.3. Carbon decomposition reaction network

To investigate how organo-mineral interactions influence SOM storage and dynamics, we modified the BAMS1 model (Riley et al., 2014) by incorporating a surface complexation model and reducing the complexity of monomer speciation (Fig. 1; Table 1). The modified BAMS1 includes a mechanistic representation of sorption processes. The reaction network consisted of (1) three groups of organic polymers (i.e., cellulose, hemicellulose, and lignin); (2) one representative simple organic monomer (or dissolved organic carbon (DOC)); (3) fungal and bacterial biomass; and (4) Dead Cell Wall Material (DCWM). However, we have not considered differences in chemical composition of DCWM between fungi and bacteria at this point, but we acknowledge the potential importance of such a distinction. Above and belowground litter and root exudates are partitioned between polymers and monomers and represent

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