

JGR Biogeosciences

RESEARCH ARTICLE

10.1029/2023JG007838

Key Points:

- Petrogenic organic C is an often poorly quantified source of soil organic C influencing its composition, age, and stability
- Using ramped combustion, we estimate that petrogenic organic C comprises 7%–9% of soil organic C in the sampled shale-derived soils
- Analyses suggest effects on soil organic C turnover are negligible when petrogenic organic C accounts for <12.5% of total soil organic C

Supporting Information:

Supporting Information may be found in the online version of this article.

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Citation:

Williams, E., & Lawrence, C. (2025). Quantifying the effect of petrogenic carbon on SOC turnover for two Rocky Mountain soils: When are petrogenic carbon corrections required? *Journal of Geophysical Research: Biogeosciences*, 130, e2023JG007838. <https://doi.org/10.1029/2023JG007838>

Received 5 OCT 2023

Accepted 17 JAN 2025

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Quantifying the Effect of Petrogenic Carbon on SOC Turnover for Two Rocky Mountain Soils: When Are Petrogenic Carbon Corrections Required?

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Abstract Petrogenic organic carbon (OC_{petro}), derived from sedimentary rocks, is an often overlooked and poorly quantified source of soil organic carbon (SOC), which may influence measured or modeled SOC composition, age, and stability. In this study, we exploited differences in thermochemical stability between OC_{petro} and biogenic SOC (OC_{bio}) using stepped elemental analysis to quantify the fractional contribution of OC_{petro} to total SOC (f_{petro}), and we conducted a sensitivity analysis to estimate the effects of OC_{petro} on modeled SOC transit times and system ages. Specifically, we compared the effects of accounting for OC_{petro} inputs in SOC turnover modeling (using SoilR) for two montane meadow soils that are underlain by Cretaceous Mancos Shale. At these sites, we estimate that OC_{petro} comprises 7%–9% of the total SOC stock ($f_{\text{petro}} = 0.07$ – 0.09). However, accounting for OC_{petro} as a mixture of inert and passive C or as completely inert C had negligible effects on SOC transit times and system ages, suggesting that there is a threshold of OC_{petro} content under which there is minimal effect on calculated SOC turnover. Based on our sensitivity analysis, we estimate this threshold to be $f_{\text{petro}} = 0.125$, further supporting that the accurate calculation of OC_{petro} remains an important factor in estimating SOC turnover.

Plain Language Summary Soils are an important reservoir of organic carbon (OC), and as such, their sensitivity and response to changing environments have the potential to impact the global carbon cycle. To understand how soil OC will respond to environmental changes, it is important to quantify both the different sources and overall amount of OC because different types of OC are cycled at different rates. OC from sedimentary rocks (OC_{petro}) is a poorly quantified component of soil OC, which has the potential to blur estimates of the composition and stability of biospheric soil OC (OC that is sensitive to environmental changes). To address this, we studied two soils that incorporate OC_{petro} from the sedimentary rocks from which the soils formed. We quantified the contribution of OC_{petro} to total soil organic carbon and characterized the effects of excluding OC_{petro} on modeled soil OC stability. Our results indicate that below a certain threshold of OC_{petro} content, OC_{petro} has negligible effect on estimates of soil OC stability.

1. Introduction

Soils contain more actively cycling carbon than the atmosphere and global terrestrial biomass combined (Jobbágy & Jackson, 2000; Stockmann et al., 2013), making them an important sink or potential source of biospheric CO_2 in response to environmental, climatic, or land use changes. The response of soils and soil carbon storage to these changes remains one of the largest uncertainties in climate feedback modeling (C. D. Jones et al., 2003, 2006; Todd-Brown et al., 2013). To model and predict the response of soil organic carbon (SOC) to environmental perturbations, it is necessary to quantify the amounts and complexities of SOC as well as the timescales of SOC storage. Uncertainties in the size, stability, and persistence of SOC stocks are partially due to unknown or unconstrained SOC turnover dynamics (turnover time, residence time, transit time, and system age). Measurement of SOC stocks and turnover dynamics is further complicated when soils are developed from organic rich sedimentary rocks (i.e., from shales and coals). Petrogenic (e.g., geogenic or fossil) organic C (OC_{petro}) from these sedimentary rocks is an often overlooked and poorly quantified fraction in soils but influences the composition, age, and stability of SOC (Agnelli et al., 2002; Kalks et al., 2021). In soils developed over sedimentary geology or those incorporating large amounts of mobilized petrogenic-derived organic matter, the contribution of OC_{petro} to SOC has a potentially large influence on calculated SOC turnover and stability (Grant et al., 2023).

Radiocarbon (^{14}C) is a critical constraint on timescale estimates of SOC cycling (turnover time, mean age, and residence time) that can improve our understanding of SOC responses to land use or environmental change

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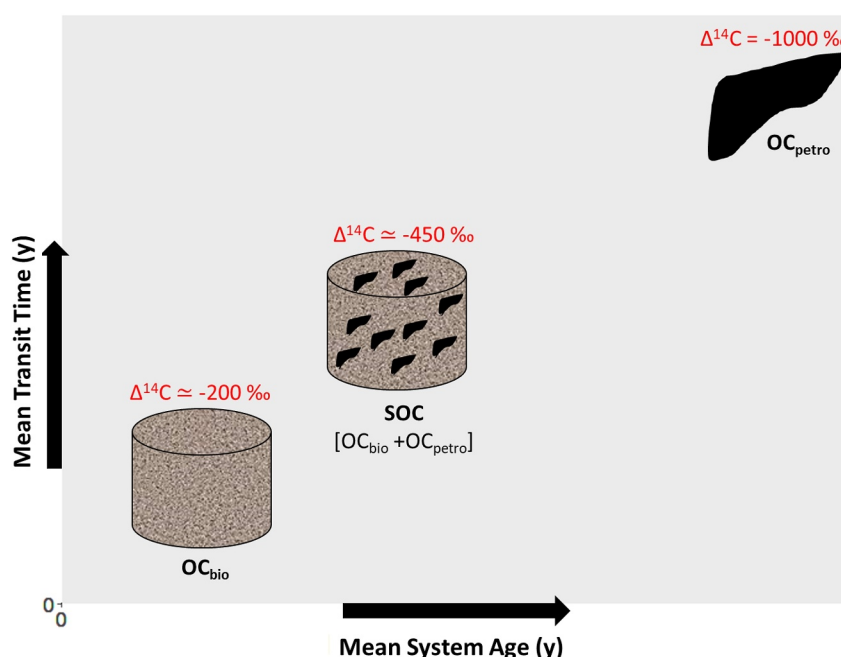


Figure 1. Conceptual hypothesis of the effect of petrogenic derived OC (OC_{petro}) on SOC transit time and system age estimates. Soil organic carbon is typically assumed to be comprised completely of biogenic OC (OC_{bio}), which can exhibit a wide radiocarbon content depending on variations of OC_{bio} inputs and persistence. By characterizing the distribution of radiocarbon in OC_{bio} , we can estimate the turnover dynamics of SOC. However, in soils developed over shale lithologies, additional inputs of OC_{petro} , which are completely depleted in radiocarbon, can distort estimates of turnover dynamics of OC_{bio} , making SOC system ages appear older and transit times appear slower. We hypothesize that accounting for the abundance of OC_{petro} will improve estimates of SOC turnover dynamics.

(Lawrence et al., 2020; Trumbore, 2009). Historically, bulk soil radiocarbon analyses were commonly used to analyze SOC turnover (Heckman et al., 2022) treating the soil as a single homogeneous pool (Torn et al., 2009); however, it is now widely recognized that soils contain heterogeneous mixtures of carbon compounds (Trumbore, 2009) that vary in composition, reactivity, and physiochemical protection and that cycle and interact with biospheric and atmospheric CO_2 at different rates. To address this, soils are often physically or chemically fractionated into pools that differ in physiochemical stability, such as density fractionation into light, particulate and heavy, mineral associated fractions (Golchin et al., 1994b; Heckman et al., 2022; Six et al., 1998; Sohi et al., 2001, 2005), size fractionation, or thermal fractionation into pools varying in thermochemical/oxidative reactivity combined with bulk, fractional, or compound specific radiocarbon analysis. Multi-pool models and approaches based on chemical or physical fractionation are commonly implemented to describe the heterogeneity of SOC stability and turnover dynamics (C. Jones et al., 2005; C. Sierra et al., 2012; C. A. Sierra et al., 2014, 2018; Trumbore, 2000).

In soils formed from parent materials containing OC_{petro} , bulk and fractional soil ^{14}C analyses may not be truly reflective of actively cycling biospheric SOC. Sedimentary rocks are a common source of OC_{petro} and cover 64% of the Earth's surface (Hartmann & Moosdorf, 2012). Of particular importance are shales, which have been estimated to comprise 25% of the global lithology (Amiotte Suchet et al., 2003). The inclusion of shale and other sedimentary rock-derived OC_{petro} , which is typically radiocarbon “dead” ($\Delta^{14}C = -1000\text{‰}$) would dilute the ^{14}C content of biospheric SOC pools (Rumpel & Kögel-Knabner, 2011), making biospheric SOC appear more ^{14}C depleted and when estimated in multi-pool soil C models older and slower cycling (Figure 1). When present, OC_{petro} may be an influencing factor in the commonly observed decrease in radiocarbon content with depth in soils especially for low-OC soils (Kalks et al., 2021).

The primary objective of this study is to quantify the abundance of OC_{petro} and its influence on modeled SOC turnover dynamics for two soils that have developed on Cretaceous Mancos Shale in central Colorado, USA. Specifically, we aim to investigate the influence of OC_{petro} on modeled SOC transit time and system age. Where system age characterizes the age structure and mean age of C stored within the soil and transit time is defined as

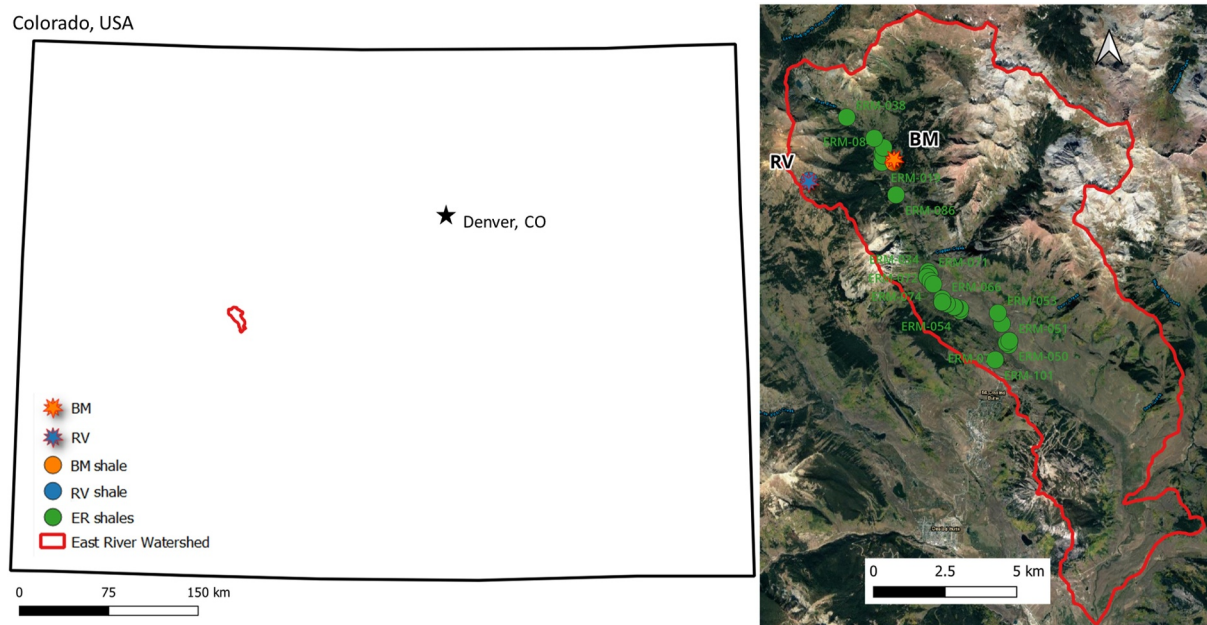


Figure 2. Sampling locations within the East River (ER) valley in the Elk Mountains of Colorado, USA. Soil and shale samples were collected from two sites: Bradley Meadow (BM) and Rock Veratrum Meadow (RV). Additional ER shale samples (green) collected by Pommer (2020) were used to help constrain heterogeneity in the OC_{petro} .

the elapsed time C atoms spend in the soil and characterizes the age structure of the output flux (respired CO₂) from the soil (C. A. Sierra et al., 2018). Because weathered petrogenic material is often physically indistinguishable and chemically inseparable from other soil materials, methods of quantification often rely on characteristic differences in the temperature of OC thermal oxidation. Geogenic or petrogenic organic matter has often undergone diagenetic or metamorphic processes, making organic carbon from those sources more thermally stable than biogenic organic matter. In this study, we exploit these general thermochemical differences in stability between petrogenic, shale-derived OC and SOC to quantify OC_{petro} content in soils. We acknowledge that the sources (e.g., types of shale) and chemical composition of geogenic or petrogenic OC are heterogeneous. Additionally, geomorphic factors may influence the mechanisms through which OC_{petro} enters soils (Hemingway et al., 2018; Horan et al., 2017). Although these variations have the potential to alter the degree to which OC_{petro} cycled in soils, they are beyond the scope of this study. We hypothesize that the inclusion of OC_{petro} in SOC turnover modeling SoilR (C. Sierra et al., 2012; C. A. Sierra et al., 2014) will result in more accurate (i.e., younger) SOC system ages and (i.e., faster) transit times (Figure 1). A second objective of this study is to quantify the effects of including OC_{petro} on model estimates of SOC transit time and system age and in doing so, identify thresholds over which OC_{petro} corrections may be necessary for accurate transit time and system age measurements. Addressing these objectives is an essential step in identifying the potential influence of OC_{petro} on model calculations of SOC transit time and system ages.

2. Methods

2.1. Site Description and Sampling

The field sites for this study are two hillslope meadows in the high-elevation, montane East River (ER) valley in the southern Colorado Rocky Mountains, USA (Elk Mountain Range): Bradley Meadow (BM) and Rock Veratrum Meadow (RV)—Figure 2. The ER valley is primarily underlain by Mancos Shale consisting of gray siltstone and shale (Morrison et al., 2012). Mancos Shale is overlain by Quaternary glacial and alluvial sediments and outcrops in several places along the ER and its tributaries (Pommer, 2020). Shales throughout the ER valley are rich in organic matter (~1%) (Morrison et al., 2012; Pommer, 2020), and previous studies (Hilton et al., 2021) have reported remarkably depleted SOC radiocarbon contents ($<-600\text{‰}$) at relatively shallow depths ($<1\text{ m}$), suggesting the potential for OC_{petro} to influence modeled SOC turnover estimates.

Table 1
Description of East River Valley Field Sites

Site	Bradley Meadow (BM)	Rock Veratrum Meadow (RV)
Location	38.98715°N 107.00391°W	38.97943°N 107.03804°W
Elevation (m)	2,987	3,466
Dominant vegetation	<i>Delphinium barbeyi</i> , <i>Potentilla pulcherrima</i> , <i>Erigeron speciosus</i> , <i>Mertensia</i> ssp., <i>Ligusticum porteri</i> , <i>Lathyrus lanszwertii</i> , <i>Veratrum californicum</i>	<i>Veratrum californicum</i> , <i>Mertensia</i> ssp.
Average soil moisture (VWC)	0.19 ± 0.08	0.22 ± 0.09
Average soil temperature (°C)	5.78 ± 4.47	4.02 ± 3.53

Note. Soil temperature and moisture (volumetric water content—VWC) values are depth weighted mean annual values (±standard deviation), averaged to a depth of 1 m from June 2016 to June 2023.

The two meadow sites differ in elevation, soil hydrologic conditions, and dominant vegetation (Table 1). BM is generally drier and warmer than the higher elevation RV. Both sites are underlain by weathered Mancos Shale saprolite (Hsu et al., 2018) and are classified as Typic Cryoborolls.

At each location, soils were sampled via hand auguring up to a depth of 100 cm, collected at 10 cm depth intervals from the surface to 40 cm and at 20 cm increments below 40 cm depth in July 2020. Additional bulk density samples were collected at the same depth increments adjacent to the sampling augur hole (<1 m distal). BM soils were sampled to 80 cm due to the presence of saprolite and coarse rock fragments at depths >80 cm. After field collection and transport to the U.S. Geological Survey laboratories in Denver, CO, soils were stored at 4°C until further processing. Soils were air-dried to constant mass and sieved to isolate the fine-fraction (<2 mm). An aliquot of the air-dried fine-fraction was ground to homogeneity using an electric ball mill grinder (Spex Sample Prep, Metuchen, NJ). Bulk density samples were dried at 105°C to constant mass, sieved (<2 mm), and weighed to obtain bulk density of the fine-fraction.

Shales were collected from exposed outcrops on Bradley Creek and Rock Creek adjacent to the BM and RV soil sampling locations (Figure 2) in June 2021. Exposed shale material was removed from the sampling surface and unexposed shale material was collected, which better reflects the composition of unweathered soil parent material. These unexposed shale materials were rinsed with ultrapure water to remove any residual dust or soil, dried at 60°C, and ground to homogeneity prior to further analysis. Additional Mancos Shale samples ($n = 39$; dried and ground) from adjacent outcrop locations in the ER valley (Figure 2) were acquired for analysis from Pommer (2020).

Aboveground vegetation was collected from the two sites in June 2021. Two 60 cm² grids were collected at each site, <5 m from the 2020 soil augur locations. Vegetation was trimmed to ground-level, dried at 60°C, weighed, and an aliquot was ground to homogeneity for further analysis.

2.2. Density Fractionation

Unground aliquots of the dried fine-fraction soils were separated into three density fractions using modified methods of Golchin et al. (1994a) and Swanston et al. (2005). Soils were fractionated using a 1.65 g/mL sodium polytungstate (SPT-0; Sometu-Europa) solution, yielding three soil fractions: a free light fraction (LF) consisting of particulate, unprotected (non-mineral associated) soil organic matter (SOM), an occluded light fraction (OF) consisting of particulate SOM physically protected within soil aggregates, and a heavy fraction (HF) consisting of SOM closely associated with soil minerals. A 20 g aliquot of unground fine-fraction soil was placed in a 250 mL centrifuge bottle with 75 mL SPT, capped, then inverted gently by hand (5×). Soils were allowed to settle undisturbed for 45 min before centrifuging at 2,583 relative centrifugal force (RCF) for 1 hr. The LF was removed by aspirating floating material from the centrifuge bottles into a sidearm flask. This material was filtered onto a 0.7 μm pre-combusted glass fiber filter (Whatman) and rinsed with ultrapure water (6×), and the residue (LF) dried for 24–48 hr at 105°C. The remaining sample pellet and SPT solution were adjusted to 75 mL with additional SPT and mixed for 1 min using a vortex mixer, sonicated (Branson Digital Sonifier 450) to attain a dispersion energy of ~440 J/mL and then centrifuged at 2583 RCF for 1 hr. The OF fraction was recovered using

the same aspiration/filtration/drying methods as for the LF. The remaining soil pellet (HF) was washed (6×) with 150 mL ultrapure water and centrifuged for 20 min at 2583 RCF for the first two rinses and 3315 RCF for the final four rinses. The resulting HF was dried for 24–48 hr at 105°C and ground to homogeneity using a ball mill grinder. A bulk soil sample (sieved, unground) was also dried at 105°C for 48 hr to account for moisture-related differences in mass recovery.

2.3. Carbon Analysis

Bulk soils, soil density fractions, aboveground plant material, and shale samples (including those collected for this study and samples previously collected by Pommer (2020) study) were analyzed for readily oxidizable organic carbon (OC₄₀₀), total inorganic carbon (TIC), and residual organic carbon (ROC) by standard methods for stepped-temperature elemental analysis (Soli TOC; Elementar, Inc.). Specifically, samples were weighed into ceramic crucibles and analyzed using a modified DIN19539GS method. First, samples were heated from ambient temperature (~25°C) to 400°C at 90°C min⁻¹ under oxidizing conditions (N₂/O₂ mixture). The temperature was held at 400°C for 6 min yielding CO₂, which is measured via an infrared gas analyzer. This fraction of sample carbon is referred to as OC₄₀₀. Next, the samplers were heated to 900°C at 110°C min⁻¹ under nonoxidizing/pyrolysis conditions (N₂) and held at 900°C for 2.5 min, yielding CO₂ corresponding to oxidation of TIC. Finally, samples were held at 900°C under oxidizing conditions (N₂/O₂ mixture) for 2.25 min yielding CO₂ corresponding to ROC. Total carbon (TC) is calculated as the sum of OC₄₀₀, TIC, and ROC, whereas total organic carbon (TOC) is equal to the sum of OC₄₀₀ and ROC. Although TIC was quantified via this approach, its discussion is beyond the scope of this study.

2.4. OC_{petro} Quantification

In this analyses, TOC is the sum of ROC and OC₄₀₀ where ROC is analytically defined as thermally recalcitrant, and OC₄₀₀ is considered relatively labile. Soils developed over organic-rich sedimentary rocks, such as shales, may contain OC from the weathering of the petrogenic lithology (OC_{petro}) in addition to inputs of recently fixed biogenic OC derived from plant and microbial decomposition and natural soil formation processes (OC_{bio}). In soils, TOC is also equal to the sum of OC_{petro} plus OC_{bio}. Therefore, the ratio of ROC:TOC (ROC_f; the fraction of OC in a soil that is relatively more thermochemically stable) is expected to vary due to differences in OC inputs (plant and microbially derived OC_{bio}, OC_{petro}, etc.) and differences in the decomposition/turnover rates of those OC sources between soils.

Similarly, we expect that the ratio of ROC:TOC (ROC_{f-petro}; the fraction of OC_{petro} in a shale sample that is relatively more thermochemically stable; Equation 1) will vary between the shales across the ER valley based on differences in their geologic history, reactivity, and weathering extent. Thus, to calculate OC_{petro} in ER soils, we make two assumptions.

First, we assume that the watershed-average ROC_{f-petro} (Equation 1) is representative and captures the average thermochemical variability of shale-derived OC_{petro} across the upper ER valley, where both ROC(%) and TOC(%) are measured on an ER shale sample.

$$\text{ROC}_{f\text{-petro}} = \frac{\text{ROC}(\%)}{\text{TOC}(\%)} \quad (1)$$

A previous study found that the ROC fraction corresponded with rock-derived OC contents in soils (Zethof et al., 2019). However, based on observational data in this study, OC_{petro} of ER shales have varying reactivity and decompose in both the OC₄₀₀ and ROC temperature ranges. Thus, in an OC_{petro}-containing ER soil, there may be joint decomposition of OC_{petro} and OC_{bio} in the OC₄₀₀ temperature range, which is accounted for using the ratio of ROC to TOC, ROC_{f-petro}.

Our second assumption is that in ER soils, OC₄₀₀ may be a mixture of OC_{petro} and OC_{bio}, but all ROC is derived exclusively from shale-derived OC_{petro} (i.e., there is no other source of refractory or petrogenic OC). In support of this assumption, we also confirmed that no ROC was observed from analyses of plant material collected from BM and RV (ROC_f = 0). Thus, for soils, we scale the ROC(%) measured in a soil by the average ROC_{f-petro} of all shale samples ($n = 41$) collected in the ER valley to yield an estimate of the concentration of SOC that is shale-derived, OC_{petro}(%):

$$OC_{\text{petro}} (\%) = \frac{ROC (\%)}{ROC_{f-\text{petro}}} \quad (2)$$

The resulting estimate of OC_{petro} , when divided by the TOC measured in the soil, yields a ratio that is an estimate (f_{petro}) of the fraction of measured SOC that is attributable to OC_{petro} :

$$f_{\text{petro}} = \frac{OC_{\text{petro}} (\%)}{TOC (\%)} \quad (3)$$

Furthermore, as we assume TOC measured in these soils derives from only two grouped sources, either OC_{petro} from shale or OC_{bio} from plant and microbially derived (biogenic) OC. We calculate OC_{bio} (%) as follows:

$$OC_{\text{bio}} (\%) = TOC (\%) - OC_{\text{petro}} (\%) \quad (4)$$

Similarly, OC_{bio} was also calculated for the heavy fraction of each soil (isolated via the density separation) using Equation 4.

2.5. Soil Incubations

Approximately 50–75 g of sieved air-dried soil were weighed into acid-washed 250 ml glass jars. Soils were wetted to ~60% water-holding-capacity using ultrapure water. The wetted soils were placed into larger incubation chambers consisting of 1 L glass jars with a layer of glass beads and water covering the bottom to prevent the soils from drying out. Lids for the incubation container were fitted with gas-tight bulkhead connectors and polyethylene tubing with two-way valves for headspace sampling and CO_2 collection. Prior to installing and sealing the lids, incubation containers were flushed with zero-air. Soils were preincubated for 24 hr to minimize the impact of sample processing on incubation results. After preincubation, jars were flushed with zero-air and sealed marking the start of the incubation period.

Headspace CO_2 concentrations in the incubation containers were measured regularly to determine when sufficient CO_2 had accumulated for radiocarbon measurements (~1.5 mg carbon). Following headspace mixing, 20–30 mL of headspace was sampled using a 60 mL syringe and analyzed for CO_2 concentration (CA-10 CO_2 analyzer, Sable Systems International, Las Vegas, NV). A sampled-equivalent volume of zero-air was injected into the jar to avoid pressure changes in the incubation chambers. When the CO_2 headspace concentration met or exceeded 1.5 mg C, the headspace was transferred (via equilibration) to pre-evacuated 400 ml metal flasks (Restek Corporation, Bellefonte, PA) for radiocarbon analysis.

2.6. Radiocarbon Analyses

Radiocarbon analyses of air-dried bulk soils, soil density fractions, and incubation CO_2 were completed at the Keck Carbon Cycle Accelerator Mass Spectrometry (KECK-AMS) facility at the University of California, Irvine in 2021. Bulk soils and HF were acid-leached to remove inorganic C prior to combustion to CO_2 . After combustion, CO_2 was purified and converted to graphite targets for ^{14}C analysis following standard Keck-AMS protocols (Xu et al., 2007). Radiocarbon content is presented in Delta notation with units of per mil (‰).

The radiocarbon content of actively cycling biogenic OC, $^{14}C_{\text{bio}}$, was calculated from bulk soil measurements, $^{14}C_{\text{toc}}$, and adjusted for the radiocarbon content of OC_{petro} , $^{14}C_{\text{petro}}$, using the following mass-balance equation:

$$^{14}C_{\text{bio}} = \frac{^{14}C_{\text{toc}} - (f_{\text{petro}} * ^{14}C_{\text{petro}})}{1 - f_{\text{petro}}} \quad (5)$$

$^{14}C_{\text{bio}}$ was also calculated for HF using Equation 5. All other terms are as defined previously.

2.7. SOC Turnover Models: System Age and Transit Time

To characterize SOC turnover dynamics, we leverage radiocarbon data to model SOC system age and transit time. System age is defined as the mean age of C atoms in the soil and characterizes the age structure of C stored within

the soil, whereas transit time is defined as the elapsed time C atoms spend in the soil and characterizes the age structure of the output flux from the soil (C. A. Sierra et al., 2018). We used the SoilR package (v1.1-23; Sierra et al., 2012; Sierra et al., 2014) to evaluate the effects of OC_{petro} on SOC transit time (function: transitTime) and system age (function: systemAge) in ER soils. We explore three different approaches for utilizing SOC concentration and isotopic data to account for the inclusion of OC_{petro} when implementing three-pool parallel models with modern C input into all pools:

1. Model P1: Measured ^{14}C and C contents were utilized without correction for OC_{petro} content. We hypothesize that model-derived system ages will be older and transit times will be slower than biogenic SOC (OC_{bio}) dynamics (Figure 1).
2. Model P2: C content and ^{14}C of the HF pool were corrected to account for estimates of OC_{petro} (Equations 4 and 5). Measured ^{14}C and C contents from LF and OF were utilized without adjustment. Implicit in this model is the assumption that all OC_{petro} is inert and therefore does not contribute to calculations of transit time or system age of the actively cycling OC_{bio} .
3. Model P3: C content and ^{14}C of the HF pool were corrected to account for OC_{petro} . However, in this model a portion of OC_{petro} is bioavailable (passively cycling) and therefore contributes to the effective (biospherically active and passively cycling) abundance and isotopic composition of C in the HF pool. Similar to Model P2, LF and OF pools were utilized without adjustment for OC_{petro} content. Partitioning of shale-derived OC_{petro} into inert and passively cycling components was based on the presence of ROC (i.e., inert) and OC_{400} (i.e., passive) C measured in shales. Although we do not assert that thermal stability is equivalent to biostability, we assume ROC, which has been used to quantify graphitic SOC (Zethof et al., 2019), requires more energy to decompose (i.e., higher temperatures) compared to the more easily oxidizable OC_{400} , and therefore, the relative abundances of these two components represent a meaningful delineation of shale-derived OC_{petro} . Thus, in this model, HF ^{14}C and C contents were adjusted based on the estimated quantity of petrogenic ROC using the following equations:

$$f_{\text{passive}} = 1 - \frac{\text{ROC}(\%)}{OC_{\text{petro}}(\%)} \quad (6)$$

$$OC_{\text{effective}}(\%) = \text{TOC}(\%) - [(1 - f_{\text{passive}}) * OC_{\text{petro}}] \quad (7)$$

$$^{14}\text{C}_{\text{effective}} = \frac{^{14}\text{C}_{\text{toc}} - \left(\frac{\text{TOC}(\%) - OC_{\text{effective}}(\%)}{\text{TOC}(\%)} * ^{14}\text{C}_{\text{inert}} \right)}{\frac{OC_{\text{effective}}(\%)}{\text{TOC}(\%)}} \quad (8)$$

where, f_{passive} is the estimated fraction of OC_{petro} passively active in SOC based on the soil ROC, $OC_{\text{effective}}$ consists of OC_{bio} combined with passive OC_{petro} . $^{14}\text{C}_{\text{effective}}$ and $OC_{\text{effective}}$ were also calculated for HF using Equations 7 and 8. $^{14}\text{C}_{\text{petro}}$ is assumed to be equal to $^{14}\text{C}_{\text{inert}}$ ($\sim 1000\text{‰}$). All other terms are as previously described.

For all models, C pools were initialized at 10% (subsoils) or 20% (surface soils) of measured C contents and we assume that $\sim 99\%$ of SOC input is routed through the LF pool (Table 2). Initial radiocarbon contents were estimated to be 0, -500 , and -800‰ for LF, OF, and HF pools, respectively. Because of assumed fast turnover, LF pools were estimated to have more modern ^{14}C contents, whereas OF and HF pool values were assumed to be more depleted, a pattern that is generally consistent with a recent metanalysis soil density fraction radiocarbon data (Heckman et al., 2022). Initial turnover constants were set to values of 0.25, 0.04, and 0.01 yr^{-1} for the LF, OF, and HF pools, respectively. Turnover constants were then estimated using a pseudorandom cost-fit optimization method that minimized of the root mean squared error (RMSE) between measured and modeled C pool size and radiocarbon content (with 0.0001 and 0.9999 yr^{-1} as lower and upper range limits of the turnover constants). The resulting best-fit turnover parameters were then used as the initial values for a Monte Carlo Bayesian optimization (1,000 iterations) to estimate uncertainty ranges of the turnover constants and to calculate SOC transit time and system age using SoilR package functions.

Each of the three models were run for each discrete soil layer corresponding to depth intervals sampled at each site. We did not include a transfer of C between depths in the model structure. For comparison between different models and sites, we aggregated the model results over two depth intervals, surface (0–30 cm), and subsoil (>30 cm).

Table 2

Model Initialization Parameters for All East River SOC Turnover Models

Model parameters	
Model structure	Parallel
Partitioning of C inputs between pools	
Pool 1—LF	0.99
Pool 2—OF	0.009
Pool 3—HF	0.001
Initial guess of pool turnover constants (yr^{-1})	
Pool 1—LF	0.25
Pool 2—OF	0.04
Pool 3—HF	0.01
Initial guess of pool ^{14}C contents (‰)	
Pool 1—LF	0
Pool 2—OF	−500
Pool 3—HF	−800
Pool C initialization—pI	
<30 cm	0.2
>30 cm	0.1
C input for each depth increment ($\text{g}\cdot\text{m}^{-2}\cdot\text{yr}^{-1}$)	$\text{Cstock}\cdot(1-\text{pI})$

Note. Parameterization was the same for all soil depths unless indicated. Additional site and depth specific model parameters (C stock and ^{14}C) are provided in Table 3.

Values for these intervals were calculated as C-abundance weighted mean transit times and mean system ages of the individual sampling increments. All models utilized a three-pool parallel structure, where LF, OF, and HF pools were constrained with density fractionation data. The models differed regarding if or how density fraction pool size and isotopic values were adjusted to account for the presence of OC_{petro} as described previously.

To better compare SOC turnover between models, we discuss C-weighted averages ($\pm$ standard error) for surface soils (0–30 cm), subsoils (>30 cm), and whole profiles. Differences in SOC turnover between models or sites were determined by one-way ANOVA with Tukey post-hoc tests ($\text{CI} = 0.9$) and differences were considered statistically significant when $p < 0.05$.

3. Results and Discussion

3.1. Characterization of East River Valley Shales

The total organic carbon (TOC) content of ER shales ($n = 41$) ranged from 0.3% to 2.02% with an average of $0.98 \pm 0.3\%$. Shale from Bradley Meadow (BM) was closer to the watershed average at $1.00 \pm 0.03\%$ TOC, whereas the TOC of shale from Rock Veratrum (RV) was lower at $0.61 \pm 0.07\%$. Stepped elemental analysis of all ER shale outcroppings generated measurable C in both the readily oxidizable (OC_{400}) and the residual oxidizable (ROC) temperature ranges. The proportions of OC oxidized in these two stability ranges, $\text{ROC}_{\text{f-petro}}$, were distinct between samples (Figure 3, Figure S1 in Supporting Information S1) likely reflecting varying geologic history, including weathering extent or possible contact metamorphism. For all ER shales, $\text{ROC}_{\text{f-petro}}$ ranged from 0.15 to 0.89 and averaged 0.56 ± 0.27 ($n = 41$). For BM and RV shales, proportionally more C from the BM shale decomposed in the OC_{400} range than for the shale from RV (BM shale $\text{ROC}_{\text{f-petro}} = 0.15 \pm 0.01$; RV shale $\text{ROC}_{\text{f-petro}} = 0.59 \pm 0.05$), suggesting that OC_{petro} from the BM shale may have a larger bioavailable fraction than shale from the RV site. This is consistent with possible contact metamorphism of RV shales from early Tertiary granitic intrusions in the eastern ER valley (Gaskill, 1991). Compared to shales collected by Pommer (2020) in the ER valley, the RV shale $\text{ROC}_{\text{f-petro}}$ value more closely resembled that of the moderately metamorphosed shales (Figure S1 in Supporting Information S1, cluster B), whereas the BM shale $\text{ROC}_{\text{f-petro}}$ value was closer to the mean values of primary Mancos Shale lithology (Figure S1 in Supporting Information S1, cluster C). Although the difference in $\text{ROC}_{\text{f-petro}}$ between RV and BM supports the use of site-specific OC_{petro} corrections, we were not able to constrain the extent of various shale lithologies at our sampling locations and thus opted to utilize average values of $\text{ROC}_{\text{f-petro}}$ for OC_{petro} estimations in soil in the ER watershed.

3.2. Estimation of OC_{petro} in ER Soils

Both RV and BM soils show expected trends of increased ^{14}C depletion, decreased SOC content, and greater HF content with depth (Figures 4a and 4b, Table 3, Table S1, Figure S3 in Supporting Information S1) with BM soils being more C rich and ^{14}C depleted than RV soils. TOC stocks (0–80 cm) were calculated to be $23.2 \text{ kg}/\text{m}^2$ at BM and $14.9 \text{ kg}/\text{m}^2$ at RV. Aboveground biomass (AGB), however, was lower at BM ($\text{BM} = 86.4 \pm 3.7 \text{ g}/\text{m}^2$; $\text{RV} = 128.9 \pm 27.2 \text{ g}/\text{m}^2$) consistent with the findings of Hsu et al. (2018). The greater TOC content of soils at BM compared to RV may be partially attributed to greater incorporation of shale-derived OC_{petro} or greater preservation of SOC at BM.

For all ER soils, stepped combustion analysis produced CO_2 for both the OC_{400} and ROC fractions, indicating the presence of OC_{petro} in accordance

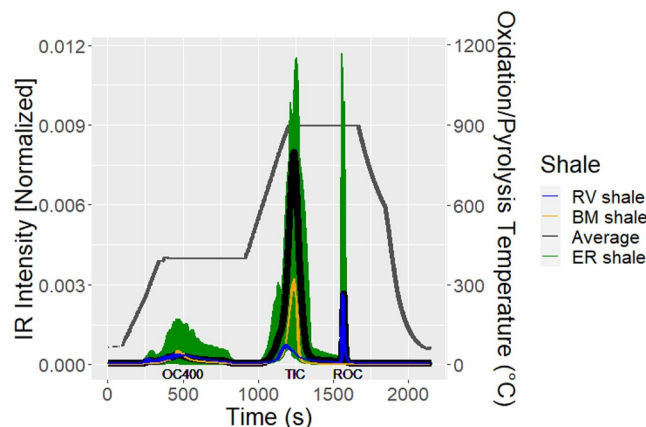


Figure 3. Stepped elemental analysis CO_2 (normalized) thermograms for shales ($n = 39$) from the East River (ER) valley (green). RV and BM adjacent shales are shown in blue and orange, respectively. The average thermogram for all shales ($n = 41$) is shown in black. Abbreviations: readily oxidizable organic carbon (OC_{400}), total inorganic carbon (TIC), residual organic carbon (ROC), infrared (IR).

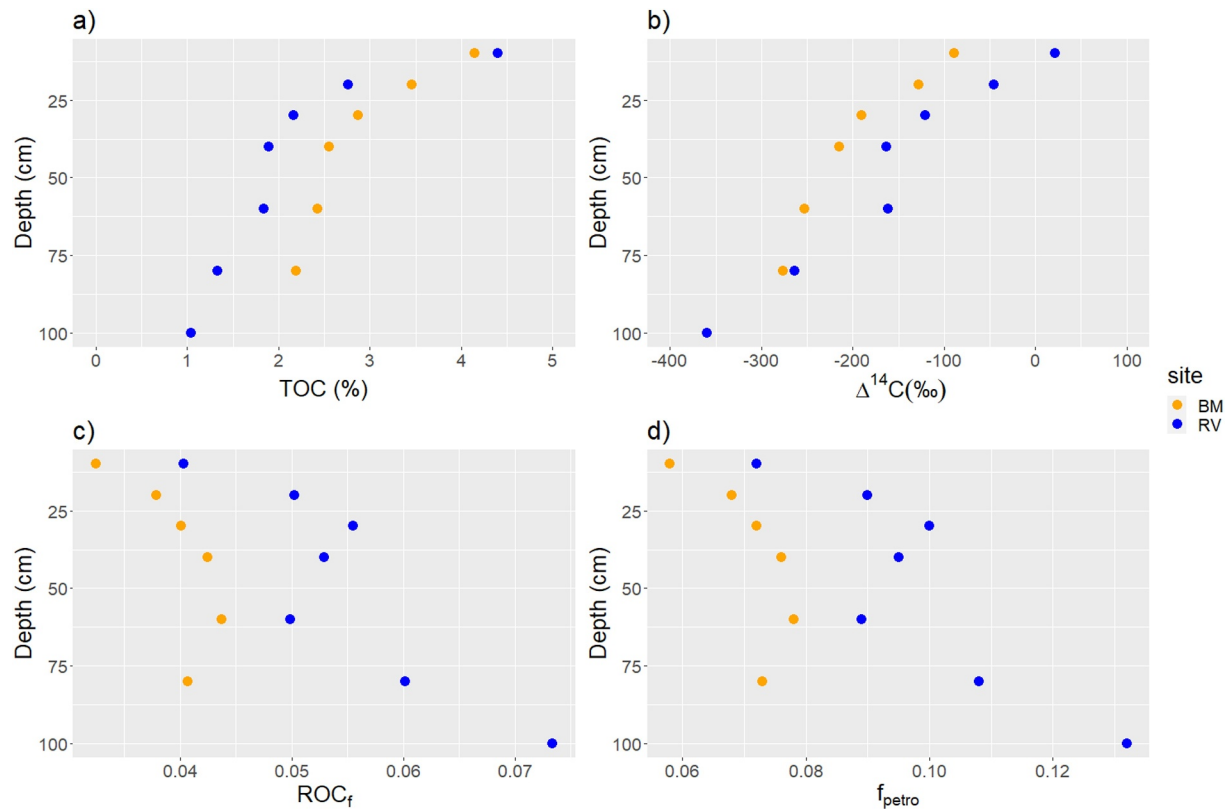


Figure 4. (a) TOC (% by mass), (b) radiocarbon content, (c) the fraction of TOC measured as ROC (ROC_f), and (d) fraction of TOC attributed to OC_{petro} (f_{petro}) from Equation 3 for bulk soils from Bradley Meadow (BM) and Rock Veratrum (RV).

with our assumptions. RV soils exhibited a larger fraction of ROC relative to the OC_{400} (Figure 4c) corresponding to greater values of ROC_f compared to BM soils. Although BM shale exhibited a greater proportion of OC_{400} compared to the RV shale, calculations of f_{petro} (Equation 3) using the watershed-average $\text{ROC}_{f\text{-petro}}$ suggest that proportionally RV soils contain more OC_{petro} compared to BM soils (Figure 4d) despite being more ^{14}C enriched

Table 3
Measured Bulk Soil and Density Fraction TOC and Radiocarbon Content by Depth Increment

Site	Depth (cm)	Bulk soil			LF			Of			HF		
		Bulk density (g/cm^3)	^{14}C (‰)	TOC (%)	^{14}C (‰)	TOC (%)	Mass (%)	^{14}C (‰)	TOC (%)	Mass (%)	^{14}C (‰)	TOC (%)	Mass (%)
BM	0–10	0.98	−88.99	4.14	30.18	24.00	3.6	−30.69	38.07	0.8	−135.65	2.84	95.6
	10–20	1.01	−128.08	3.46	7.11	25.39	1.3	−81.94	31.05	0.6	−158.68	2.57	98.1
	20–30	1.15	−190.60	2.87	−57.11	28.14	0.5	−180.27	31.20	0.4	−206.72	2.41	99.1
	30–40	1.15	−214.43	2.55	−1.00	25.84	0.3	−216.44	28.31	0.4	−225.33	2.21	99.3
	40–60	1.02	−252.75	2.43	−41.96	36.30	0.3	−296.28	26.77	0.5	−272.77	1.92	99.3
	60–80	1.01	−276.29	2.19	−67.46	32.08	0.3	−305.80	42.45	0.1	−291.07	1.89	99.6
RV	0–10	0.79	21.72	4.40	84.44	9.25	8.4	108.04	30.77	0.9	−19.52	2.98	90.7
	10–20	0.85	−45.82	2.76	223.13	33.50	1.5	34.15	29.87	0.3	−98.69	2.12	98.2
	20–30	0.81	−120.41	2.16	115.34	17.11	0.7	−14.01	38.92	0.1	−141.41	1.70	99.3
	30–40	0.81	−162.75	1.89	77.99	25.42	0.4	−79.15	29.31	0.2	−186.97	1.64	99.4
	40–60	0.9	−161.64	1.84	73.12	27.37	0.3	−23.28	20.87	0.1	−169.30	1.59	99.6
	60–80	0.93	−263.36	1.33	77.45	26.89	0.1	−111.59	34.21	0.1	−282.62	1.19	99.8
	80–100	0.93	−359.51	1.04	46.29	29.59	0.1	−147.94	32.79	0.1	−356.45	0.99	99.8

Note. Bulk density is of the fine (<2 mm) soil fraction.

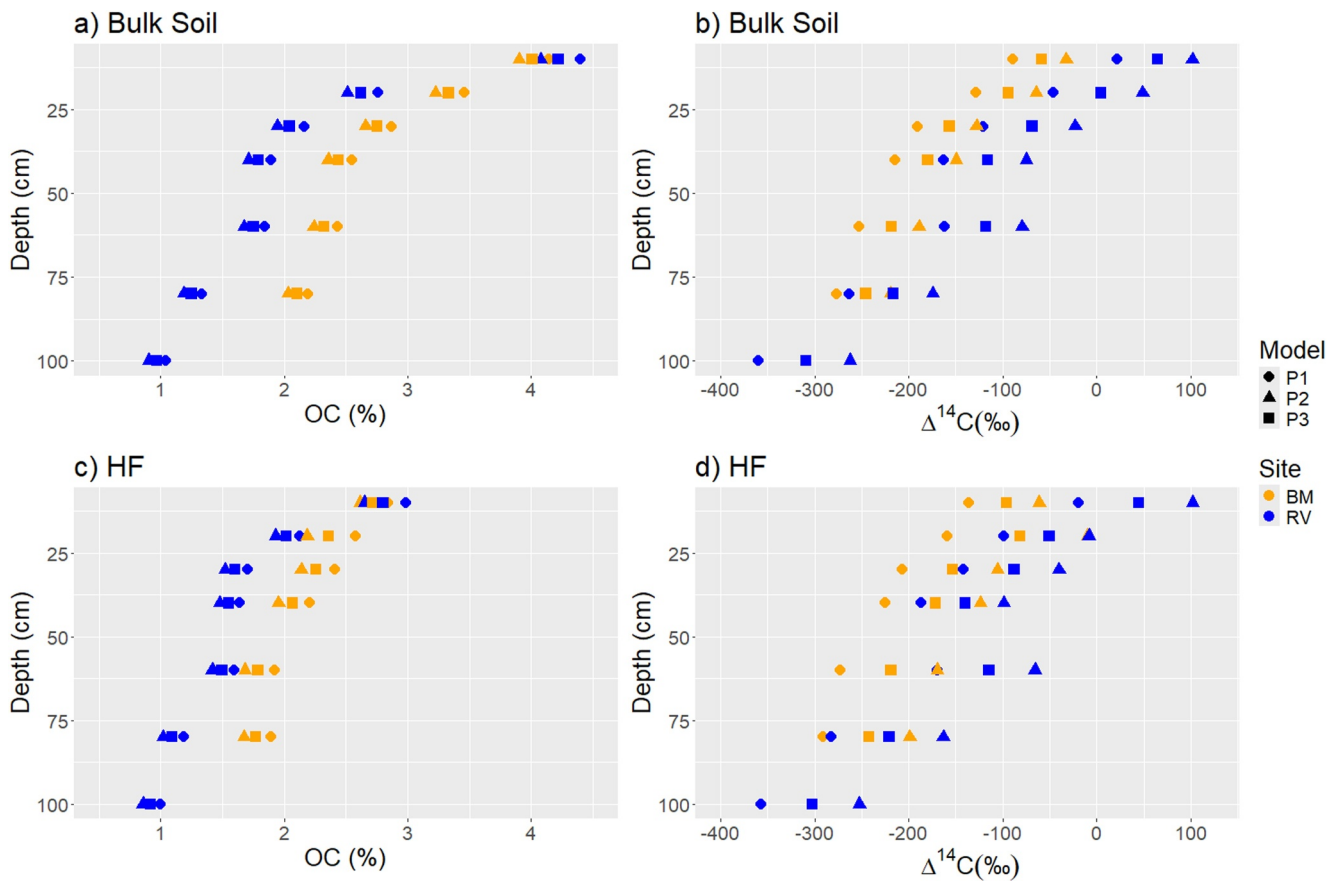


Figure 5. OC (% by mass) and radiocarbon content for bulk soils (a–b) and HF (c–d) from Bradley Meadow (BM) and Rock Veratrum (RV). Model P1 shows measured TOC and ^{14}C . Model P2 shows OC_{bio} and $^{14}\text{C}_{\text{bio}}$ from Equations 4 and 5, which assume all OC_{petro} is inert. Model P3 shows $\text{OC}_{\text{effective}}$ and $^{14}\text{C}_{\text{effective}}$ from Equations 7 and 8, which assume OC_{petro} is a mixture of passive and inert C.

than BM soils. However, because of greater TOC contents in BM soils, the OC_{petro} stock (0–80 cm) was calculated to be 1.6 kg/m² or 7% of the TOC stock ($f_{\text{petro}} = 0.07$). Whereas, at RV, the OC_{petro} stock (0–80 cm) was 1.3 kg/m² or 9% of the TOC stock ($f_{\text{petro}} = 0.09$). Estimates of f_{petro} from BM are much lower than estimates based on rhenium content by Hilton et al. (2021) in which $f_{\text{petro}} = 0.42$ at the same meadow location (Figure S3 in Supporting Information S1). This discrepancy could be due to our utilization of a watershed-averaged $\text{ROC}_{f\text{-petro}}$ instead of a site-specific value or to heterogeneity of OC_{petro} incorporation in soils across the meadow. However, we note that the incorporation of larger values of f_{petro} (>0.28 at the surface and >0.45 at depth at BM; Figure S3 in Supporting Information S1) lead to unrealistic HF- $^{14}\text{C}_{\text{effective}}$ and HF- $^{14}\text{C}_{\text{bio}}$ values that exceeded the maximum HF- ^{14}C value (111.58‰) from the ISRaD database (Lawrence et al., 2020). Additionally, in a synthesis study that utilized the ISRaD database, Grant et al. (2023) estimated $f_{\text{petro}} = 0.38$ to be the average maximum amount of OC_{petro} permissible in sedimentary-rock derived soils. For all soil depths at BM and RV, our estimates of f_{petro} are below these maximum f_{petro} estimates. Although we are confident we have not overestimated OC_{petro} content, it is possible that we underestimated it especially at the BM site where $\text{ROC}_{f\text{-petro}}$ differed greatly from the regional average (Figure 3).

By adjusting soil C and ^{14}C data assuming that all OC_{petro} is inert ($f_{\text{inert}} = 1$; Model P2; Equations 4 and 5), both RV and BM soils exhibit more depleted $^{14}\text{C}_{\text{bio}}$ and decreased OC_{bio} content with depth (Figure 5; Table S1 in Supporting Information S1). After this adjustment, profile-scale OC_{bio} stocks (0–80 cm) totaled 21.5 kg/m² at BM and 13.5 kg/m² at RV. Similarly, by treating OC_{petro} as including a mixture of passive and inert C ($f_{\text{inert}} = 0.56$; Model P3; Equations 7 and 8) both RV and BM soils continue to exhibit expected increased $^{14}\text{C}_{\text{effective}}$ depletion and decreased $\text{OC}_{\text{effective}}$ content with depth (Figure 5; Table S1 in Supporting Information S1). In this treatment, the $\text{OC}_{\text{effective}}$ stock (0–80 cm) was 22.3 kg/m² at BM and 14.1 kg/m² at RV, where passive OC_{petro} is estimated to

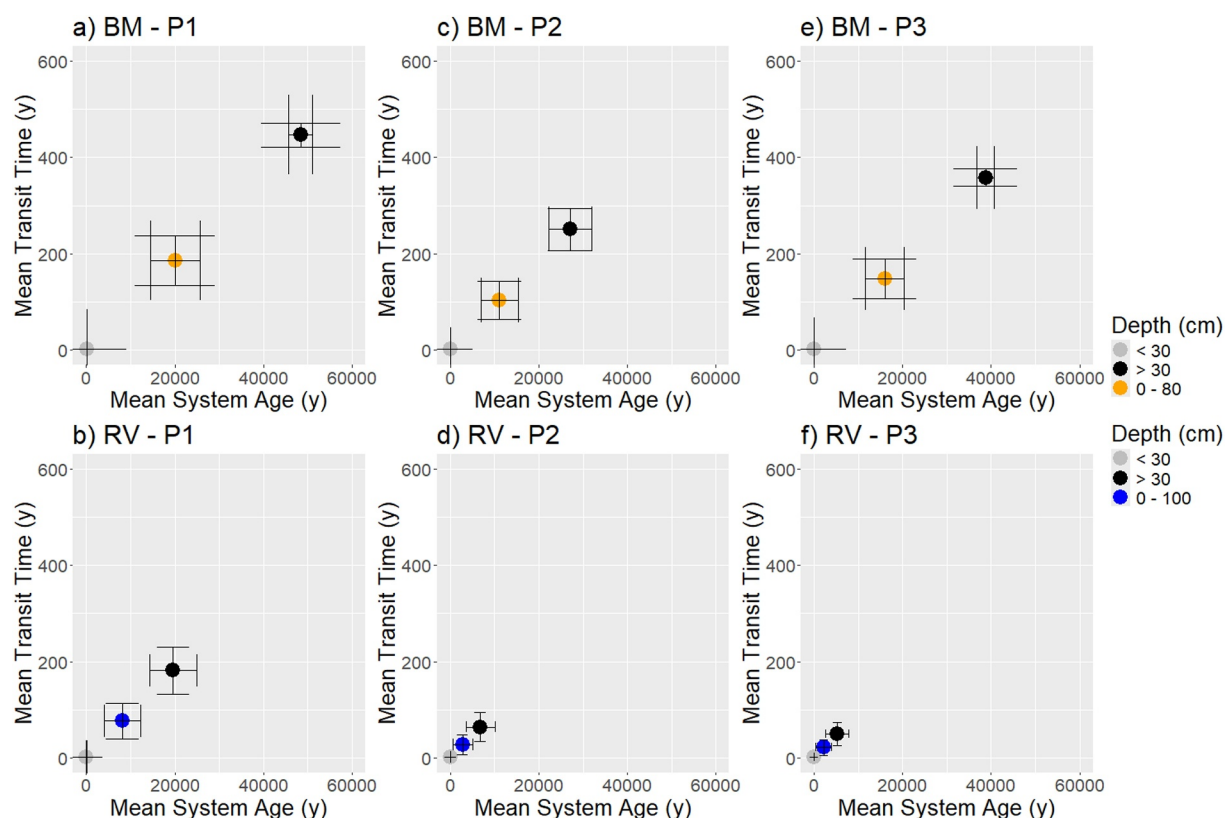


Figure 6. Modeled SOC transit times and system ages ($\pm$ standard error) for Bradley Meadow (BM) and Rock Veratrum (RV) soils. Model P1 (a–b) does not account for OC_{petro} , model P2 (c–d) treats all OC_{petro} as inert, and model P3 (e–f) treats OC_{petro} as a mixture of inert C and passive C. Surface soils (<30 cm) are gray, subsoils (>30 cm) are black, and profile averages are in orange (BM) and blue (RV).

contribute 0.7 and 0.6 kg/m² to TOC at BM and RV, respectively. As expected, compared to the P1 model, differences in C content and ¹⁴C from model P3 are less than from model P2 as a portion of the OC_{petro} (f_{passive}) is assumed to cycle with the HF.

3.3. SOC Turnover Modeling: Effects of OC_{petro}

Without accounting for the presence of OC_{petro} (Model P1), modeled transit times and system ages increased with depth at both locations (Figures 6a and 6b, Table S1 in Supporting Information S1). In surface soils (0–30 cm), transit times were not different between sites ($p = 0.81$), averaging 2 ± 0.03 y at Bradley Meadow (BM) and 2 ± 0.1 y at Rock Veratrum (RV). However, surface soil system ages were greater at BM ($p = 0.04$), averaging 43 ± 2 y at BM and 17 ± 2 y at RV. In subsoils (>30 cm), transit time averages increased, compared with the surface horizons, and were slower at BM ($p = 0.03$), averaging 447 ± 25 y at BM and 182 ± 49 y at RV. Similarly, subsoil system ages increased compared with surface soils and were greater at BM ($p = 0.03$), averaging $48,431 \pm 2,701$ y at BM and $19,551 \pm 5,298$ y at RV. Averaged over the entire profile, Model P1 based SOC transit times were estimated at 186 ± 51 y at BM and 77 ± 37 y at RV, and profile system age estimates were $20,013 \pm 5,604$ y at BM and $8,143 \pm 4,038$ y at RV.

Model P1 does not explicitly account for the inclusion of radiocarbon dead OC_{petro} estimated for the ER soils. We hypothesized that by not accounting for OC_{petro} , we would overestimate the amount and underestimate the radiocarbon content of bioavailable OC in the HF. Subsequently, this would result in an underestimation of the modeled turnover constant for this pool because first-order kinetics dictates that, all else being equal, a smaller flux from a more radiocarbon depleted endmember would be required to yield the same mixture of respired CO₂ from soil incubations. Although the HF pool is typically the most radiocarbon depleted and thought to be the most stable SOC fraction, studies have demonstrated that HF is itself a mixture of younger and older components (Kögel-Knabner et al., 2008; Schrumpf & Kaiser, 2015; Swanston et al., 2005). This suggests a continuum of

SOC characteristics within the HF pool, and in the case of soils known to contain large amounts of OC_{petro} , there is a case for further partitioning of the HF pool or otherwise accounting for such heterogeneity.

By treating all OC_{petro} as inert (Model P2) modeled transit times and system ages increased with depth at both locations (Figures 6a and 6b, Table S1 in Supporting Information S1) as expected. In surface soils (0–30 cm), transit times were again similar between the two sites ($p = 0.94$), averaging 2 ± 0.04 y at BM and 2 ± 0.1 y at RV. Surface soil system ages were not significantly different between the sites ($p = 0.13$), averaging 22 ± 2 y at BM and 5 ± 0.8 y at RV. In subsoils (>30 cm), transit time averages increased, compared with the surface horizons, but were still similar between the two sites ($p = 0.15$), averaging 251 ± 44 y at BM and 64 ± 30 y at RV. Similarly, subsoil system ages increased compared with surface soils but were not significantly different between the sites ($p = 0.15$), averaging $27,123 \pm 4,791$ y at BM and $6,793 \pm 3,267$ y at RV. Averaged over the entire profile, Model P2 SOC transit times were similar between the sites, averaging at BM at 104 ± 39 y and 28 ± 20 y at RV ($p = 0.23$), similarly profile system age estimates were not different between sites ($p = 0.23$) at $11,133 \pm 4,277$ y at BM and $2,795 \pm 2,223$ y at RV. However, at the profile-scale, neither the transit time nor system age from the P2 model were statistically different from the P1 model ($p = 0.30$; Table S2 in Supporting Information S1). In a comparable study using the RothC model, Finke et al. (2019) also determined that accounting for inert organic matter did not improve SOC turnover estimates in a California chronosequence but suggested that the inclusion of an additional slower/passive cycling pool could improve SOC modeling.

Although OC_{petro} is typically considered to have intrinsic recalcitrance, previous studies on shale weathering and decomposition have demonstrated that shale-derived OC_{petro} is not completely inert (Hemingway et al., 2018; Matlakowska et al., 2010; Matlakowska & Sklodowska, 2011; Petsch et al., 2001, 2005; Wengel et al., 2006) and can be decomposed by environmental conditions and microorganisms present in soils and sediments. Additionally, OC_{petro} is a continuum of OC compounds whose reactivities depend upon present environmental conditions as well as geologic history (Petsch, 2014). Although this range of thermochemical reactivities may be reflected in the range of $ROC_{\text{f-petro}}$ values of ER shales (Figure 3), respired $^{14}\text{CO}_2$ from ER soils (Figure S4 in Supporting Information S1) did not directly indicate the oxidation of OC_{petro} - as root activity and oxidation of more recent OC_{bio} is expected to muffle the very slow production of $\text{CO}_{2\text{-petro}}$ (Tune et al., 2023). However, it remains plausible that some portion (f_{passive}) of OC_{petro} may contribute to slow-cycling SOC pools depending upon the shale history/type.

In the P3 model, the presence of both inert and passive OC_{petro} is addressed using the measured parameter $ROC_{\text{f-petro}}$ to determine the amount of OC_{petro} to exclude from the adjusted HF pool. In this model, SOC transit times and system ages still increased with depth at both locations as expected (Figures 6e and 6f, Table S1 in Supporting Information S1). In surface soils (0–30 cm), transit times were similar between sites ($p = 0.69$), averaging 2 ± 0.03 y at BM and 2.4 ± 0.1 y at RV. Surface soil system ages were also similar between sites ($p = 0.05$), averaging 33 ± 1.7 y at BM and 22 ± 1.3 y at RV. In subsoils (>30 cm), SOC transit time averages increased at depth but were greater at BM ($p < 0.01$), averaging 357 ± 18 y at BM and 50 ± 24 y at RV. Subsoil system ages also increased at depth and were also greater at BM ($p < 0.01$), averaging $38,741 \pm 1,973$ y at BM and $5,278 \pm 2,608$ y at RV. However, when averaged over the entire profile, using Model P3, SOC transit times were not statistically different between sites ($p = 0.07$; Table S2 in Supporting Information S1) and are estimated at 148 ± 41 y at BM and 22 ± 16 y at RV, similarly profile system ages were also not statistically different between sites ($p = 0.07$) and were estimated at $15,951 \pm 4,444$ at BM and $2,169 \pm 1,763$ y at RV. Similarly, neither the transit time nor system age from the P3 model were statistically different from the P1 model ($p = 0.47$) at the profile scale.

Overall, accounting for passive or inert OC_{petro} (P2 and P3 models) had no significant effect on SOC transit time and system age estimates in ER surface soils or subsoils nor at the profile scale, resulting in statistically similar SOC turnover estimates when compared to the P1 model.

3.4. Site Differences Between ER Soils

SOC transit times and system ages from all three models fit within the range of global mean values observed by C. A. Sierra et al. (2018). For all ER soils, system ages were older than transit times (Figure 6), indicating a “non-retentive” system (C. A. Sierra et al., 2018) in which the majority of OC enters and leaves the soil system in a relatively short time (fast transit times), but the OC that remains stays in the soil for a long time (old system ages).

This is indicative of input and output fluxes occurring at relatively close distances between each other, and storage is physically separated from them (Bolin & Rodhe, 1973; C. A. Sierra et al., 2018).

Although there are small differences in SOC cycling at the subsoil and surface soil levels using the P1 and P3 models (Table S2 in Supporting Information S1), at the profile scale, there was no difference in SOC turnover between Bradley Meadow (BM) and Rock Veratrum (RV). This result was unexpected based on site-level environmental and expected SOM compositional differences. For example, a previous study comparing the chemical composition of SOC from these sites found that the BM are predominantly composed of polysaccharides, whereas the RV site have more substantial portions of carbonyl, phenolic, or aromatic carbon (Hsu et al., 2018), suggesting that SOC is more chemically labile at BM compared with RV. Similarly, the lower elevation site, BM, is warmer for longer periods of the year compared to RV, which has a shorter growing season due to prolonged snow cover, suggesting slower or more limited soil microbial activity at RV. However, during laboratory incubations, RV SOC respiration rates were initially slower than for BM soils, but over the course of the incubation (and at depth), RV respiration was equivalent to or surpassed BM SOC (Figure S4b in Supporting Information S1). This may suggest faster SOC cycling at RV despite environmental differences, corresponding with younger system ages and faster transit times in RV subsoils (P1 model). However, at the profile scale, our results suggest that SOC cycling rates are similar between BM and RV as inputs (above and below-ground biomass and microbial inputs) and outputs (soil respiration—Figure S4 in Supporting Information S1) are relatively similar between the sites and are not affected by the presence of the small amounts of OC_{petro} as the remineralization of OC_{petro} likely contributes very little to the output flux.

Although we are confident that we did not overestimate OC_{petro} for these soils based on radiocarbon constraints, it is plausible that OC_{petro} content was underestimated. The watershed averaged $ROC_{\text{f-petro}}$ was much larger than what was measured for the BM shale and suggests that OC_{petro} may have been more underestimated for BM soils than for RV soils. Additionally, the f_{petro} determined using the watershed average $ROC_{\text{f-petro}}$ was much lower than f_{petro} determined by Hilton et al. (2021) at BM (Figure S3 in Supporting Information S1), again suggesting possible underestimation of OC_{petro} at that location. However, the rhenium estimation of f_{petro} was above our calculated f_{petro} maximum values at depths >50 cm and would have resulted in overestimation of OC_{petro} . Similarly, mixing model estimates of f_{petro} overlapped or exceed our calculated maximum f_{petro} max values at all depths and would have also resulted in overestimations of OC_{petro} (Figure S3 in Supporting Information S1). Additionally, using the measured $ROC_{\text{f-petro}}$ for the BM shale would have also resulted in overestimations of OC_{petro} (confirmed by unrealistic radiocarbon values greater than the maximum plausible $HF^{14}C$ content). This suggests that the OC_{petro} estimation methods employed in this study may not be suitable for relatively labile (greater proportions of OC_{400} compared to ROC ; smaller $ROC_{\text{f-petro}}$) petrogenic materials, than as these materials may have similar relative thermochemical decomposition/oxidation distributions as soils. The oxidation of petrogenic materials at 400°C also implies that ROC may not be representative of the entire “residual” or “refractory” SOC pool, and it is plausible that during pyrolysis of TIC (400–900°C), there was also co-pyrolysis of OC_{petro} (Hemingway et al., 2018), potentially also resulting an underestimation of TOC and OC_{petro} ; therefore, caution should be used when assigning meaning to the OC_{petro} or ROC pools without prior analytical confirmation with known end-members.

3.5. OC_{petro} Sensitivity Analysis: When Does OC_{petro} Need to Be Accounted for?

Transit time characterizes the age structure of the output flux from the soil system and depends on the cycling rates of each pool and transfers between them, whereas system age characterizes the age structure of the carbon stored within the soil system and depends on the total amounts of C inputs/outputs from each pool (C. A. Sierra et al., 2018). We expected that both parameters would be affected by the presence of OC_{petro} in soils; however, it is unknown how much OC_{petro} is required to have a measurable effect on SOC turnover estimates. Given the nonsignificant shifts in transit time and mean system age calculations observed for our study sites, we conducted a model sensitivity analysis to determine what values of f_{petro} and f_{inert} would result in significant impacts on SOC turnover calculations.

In the sensitivity analysis, f_{petro} [0, 0.0625, 0.125, 0.25, 0.375, and 0.5] and f_{inert} [0–0.95: increments of 0.2375] were varied for one surface soil and one subsoil from each ER site (RV 10–20 cm, RV 60–80 cm, BM 10–20 cm, BM 60–80 cm) using the model parameters listed in Table 2. Scenarios where $f_{\text{petro}} = 0$ and OC_{petro} is not accounted for in SOC turnover are equivalent to the P1 model. In these scenarios, there is no effect on system age

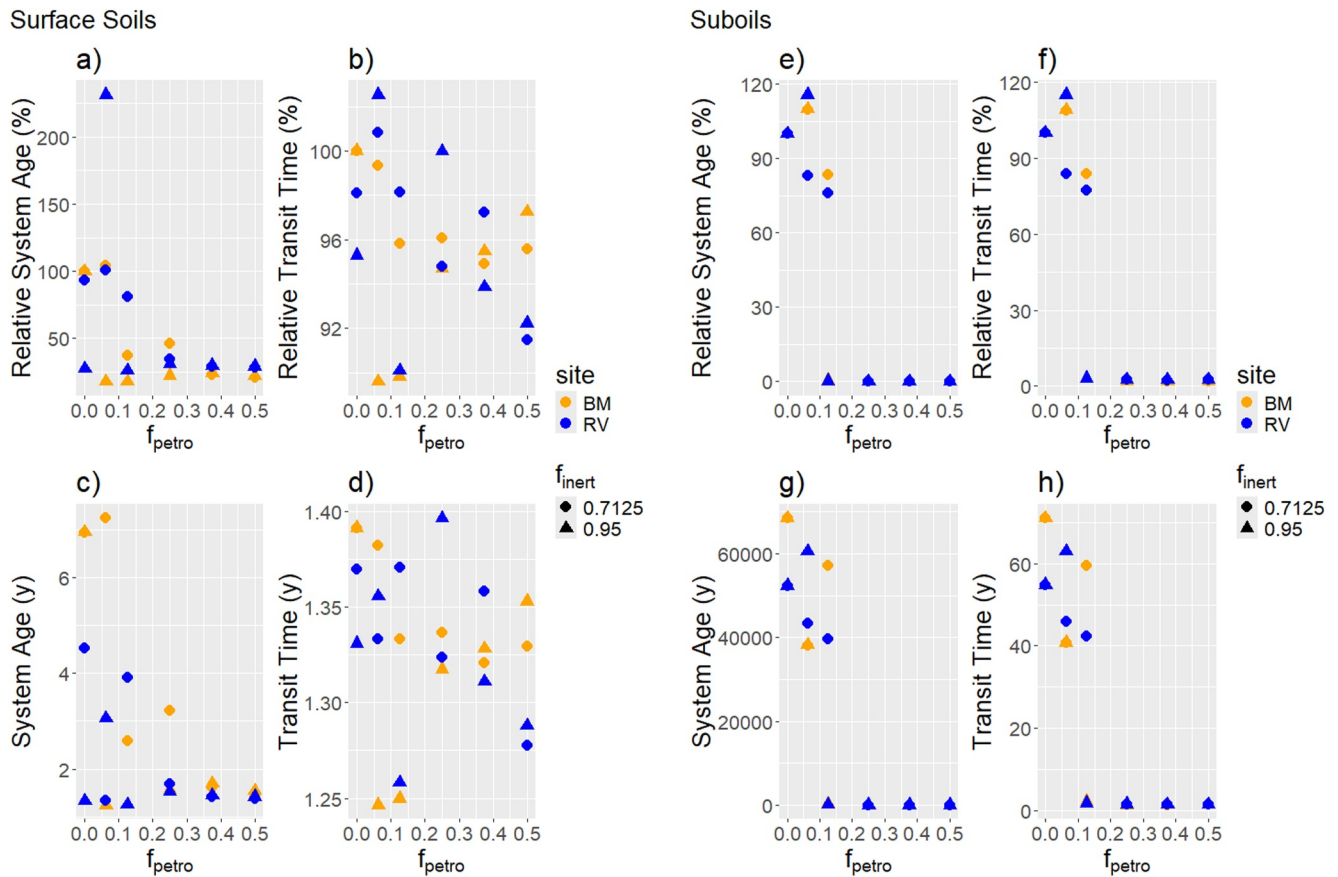


Figure 7. Sensitivity analysis of modeled SOC system age and transit time estimates to OC_{petro} for surface soils (BM 10–20 and RV 10–20 cm; a–d) and subsoils (BM 60–80 cm and RV 60–80 cm; e–h) with varying f_{petro} and f_{inert} . Full model output results are listed in Table S3 in Supporting Information S1.

or transit time with changing f_{inert} as there is no change in any of the OC pools (Table S3 in Supporting Information S1).

Scenarios where $f_{\text{petro}} > 0$ and $f_{\text{inert}} \cong 1$ are equivalent to the P2 model, in which OC_{petro} is completely inert. In this scenario, increasing f_{petro} increasingly enriches $HF-^{14}C_{\text{bio}}$, compared to the unadjusted soil (P1 model), as more OC_{petro} is excluded from the HF pool (Table S3 in Supporting Information S1). In subsoils, there are substantial effects on system age and transit time estimates as $HF-OC_{\text{bio}}$ pool sizes decrease with increasing f_{petro} , exhibiting a 97%–99% decrease in transit time and system age when $f_{\text{petro}} > 0.125$ (Figure 7, Tables S3 and S4 in Supporting Information S1). In surface soils, the effect of OC_{petro} in system age and transit time is much smaller, with no statistically significant changes in system age or transit time (Table S4 in Supporting Information S1), likely due to the already low estimates. At $f_{\text{petro}} > 0.25$ for surface soils and $f_{\text{petro}} > 0.375$ for subsoils, HF exceeded our hypothesized upper limit of $HF-^{14}C_{\text{bio}}$ (111.58‰) suggesting that the resulting transit times and system ages are derived from these f_{petro} values are unrealistic. Finally, in all other scenarios where $f_{\text{petro}} > 0$ and $f_{\text{inert}} = 0$ –0.99, are representative of model P3. If $f_{\text{petro}} > 0$ and OC_{petro} is completely biospherically active ($f_{\text{inert}} = 0$), OC_{petro} would cycle simultaneously within OC_{bio} (Table S3 in Supporting Information S1). In this scenario, increasing f_{petro} increasingly depletes $HF-^{14}C_{\text{effective}}$ as more OC_{petro} is forced to cycle within the HF pool. However, in most scenarios, there is negligible effect on system age and transit time estimates as HF $OC_{\text{effective}}$ pool sizes remain the same. This scenario of completely labile or biospherically active OC_{petro} is not reflected in SOC respiration from ER soils and is not expected to occur in most soil environments as OC_{petro} has intrinsic physical and chemical stability. However, if $f_{\text{petro}} > 0$ and OC_{petro} is not completely biospherically active nor completely inert ($f_{\text{inert}} = 0.01 \sim 0.99$), passive OC_{petro} would still cycle simultaneously within HF $OC_{\text{effective}}$ but increasing f_{petro} would enrich $HF-^{14}C_{\text{effective}}$ as OC_{petro} is excluded from the HF pool (Table S3 in Supporting Information S1) with transit times and system ages generally decreasing with increasing f_{petro} or f_{inert} and these changes being greater for subsoils compared to surface soils.

Combined these sensitivity analyses demonstrate that even minimal inputs of OC_{petro} ($f_{\text{petro}} \geq 0.125$) can substantially affect modeled SOC transit times and system ages (Figure 7, Tables S3 and S4 in Supporting Information S1), although the actual f_{petro} threshold may be between 0.0625 and 0.125. The sensitivity analysis also suggests that the effects on (i.e., reduction in) system age and transit time increase as f_{inert} increases. These results demonstrate that the accurate calculation of f_{petro} (and possibly f_{inert}) remains the most important factor in determining if SOC turnover estimates require OC_{petro} corrections.

4. Conclusions

Using a ramped combustion/pyrolysis method, we estimate that OC_{petro} comprises 7% of the TOC stock at BM and 9% at RV. However, this method likely underestimates the contribution of OC_{petro} and should be used with caution. Accounting for OC_{petro} as either completely inert (Model P2) or a mixture of inert and passive C (Model P3) had no effect on SOC transit times or system ages because the contribution of OC_{petro} to the overall SOC stock was relatively small. Our sensitivity analysis suggested that for $f_{\text{petro}} < 0.125$, there is a negligible effect on modeled transit times and system ages. The sensitivity analysis also suggests that the effects on (i.e., reduction in) system age and transit time increase as f_{inert} increases and imply that the accurate calculations of f_{petro} and f_{inert} (possibly through improved thermal analyses and biochemical incubations, respectively) remain the most important factors in determining if SOC turnover estimates require OC_{petro} corrections. Thus, we propose a minimum f_{petro} limit of 0.125 over which accounting for OC_{petro} is expected to result in significant differences in transit time and system age that would have a substantial impact on SOC modeling.

Data Availability Statement

Underlying observational data employed in this study is available in Williams and Lawrence (2025, <https://doi.org/10.5066/P9NI8OWJ>). The R script used in this study is included in Text S1 in Supporting Information S1.

Acknowledgments

This study was funded by the Climate Research and Development and Land Change Science programs of U.S. Geological Survey Ecosystems Mission Area. We thank Dr. Carlos Sierra for constructive comments on an early version of this manuscript. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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