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Soils' dirty little secret: Depth-based comparisons can be inadequate for quantifying changes in soil organic carbon and other mineral soil properties

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Abstract

Quantifying changes in soil organic carbon (SOC) stocks and other soil properties is essential for understanding how soils will respond to land management practices and global change. Although they are widely used, comparisons of SOC stocks at fixed depth (FD) intervals are subject to errors when changes in bulk density or soil organic matter occur. The equivalent soil mass (ESM) method has been recommended in lieu of FD for assessing changes in SOC stocks in mineral soils, but ESM remains underutilized for SOC stocks and has rarely been used for other soil properties. In this paper, we draw attention to the limitations of the FD method and demonstrate the advantages of the ESM approach. We provide illustrations to show that the FD approach is susceptible to errors not only for quantifying SOC stocks but also for soil mass-based properties such as SOC mass percent, C:N mass ratio, and δ^{13}C. We describe the ESM approach and show how it mitigates the FD method limitations. Using bulk density change simulations applied to an empirical dataset from bioenergy cropping systems, we show that the ESM method provides consistently lower errors than FD when quantifying changes in SOC stocks and other soil properties. To simplify the use of ESM, we detail how the method can be integrated into sampling schemes, and we provide an example R computer script that can perform ESM calculations on large datasets. We encourage future studies, whether temporal or comparative, to utilize sampling methods that are amenable to the ESM approach. Overall, we agree with previous recommendations that ESM should be the standard method for evaluating SOC stock changes in mineral soils, but we further suggest that ESM may also be preferred for comparisons of other soil properties including mass percentages, elemental mass ratios, and stable isotope composition.

KEYWORDS
carbon accounting, carbon stocks, carbon-to-nitrogen ratio, equivalent soil mass, soil isotopic composition, soil organic carbon

1 | INTRODUCTION

Soils play a critical role in regulating the global carbon cycle, yet the impacts of land management practices, such as the widespread planting of perennial bioenergy crops (Whitaker et al., 2018), and global change on soil organic carbon (SOC) stocks remain highly uncertain (Bradford et al., 2016; Sulman et al., 2018). Accurately quantifying temporal changes in soil properties such as SOC stocks

presents a potentially underappreciated set of complications (Boone, Grigal, Sollins, Ahrens, & Armstrong, 1999; Paustian et al., 2019). Most longitudinal studies use a fixed depth (FD) approach to assess changes in SOC stocks, whereby soil samples are compared at consistent soil depth intervals (e.g., 0–10 cm) at two or more time points. Although the FD approach is intuitive and convenient, the potential drawbacks for assessing changes in SOC and other elemental stocks have long been known (e.g., Nye & Greenland, 1964). Specifically, when bulk density varies through time, as might be expected with various management practices (e.g., tillage), then FD-based comparisons will be incorrect because the sampled mass of soil per unit area also varies through time (Wuest, 2009). Similarly, if soil organic matter (SOM) stocks change through time, FD measurements may be inaccurate because the volume of soil is also likely to change (Henzell, Fergus, & Martin, 1967; Skene, 1966). As an alternative to FD, the equivalent soil mass (ESM) approach relies on comparisons to a consistent mass of mineral soil, and thus measurements are not adversely affected by changes in bulk density or SOM (Ellert & Bettany, 1995). Recent publications from the IPCC, FAO, and others have highlighted the use of ESM for assessing SOC stock dynamics (FAO, 2019; IPCC, 2019; Smith et al., 2019), but to date ESM has not been widely implemented (Cardinael et al., 2018).

Although the potential for FD-based errors when calculating stocks of SOC and other elements has been well-documented (e.g., Ellert & Bettany, 1995; Ellert, Janzen, & Entz, 2002; Wendt & Hauser, 2013), there has been little discussion of FD errors in relation to temporal or comparative measurements of other soil mass-based properties (Lee, Hopmans, Rolston, Baer, & Six, 2009; Skene, 1966; Wuest, 2009). For example, SOC mass percentages (g SOC/100 g soil; frequently called "SOC concentration"), C:N mass ratios (g SOC/g N), and C stable isotope composition (δ^{13}C) are often used to infer SOM characteristics including origin, decomposition stage, and mean residence time (Paul, 2016; Schrumpf et al., 2013). Unlike soil elemental stocks, FD-based quantification of these soil mass-based properties does not inherently require concomitant assessment of soil bulk density, and thus it might be assumed that bulk density changes do not affect the quantification of these soil properties. However, when soil bulk density varies through time, the mass of soil sampled per unit area to a FD also changes regardless of whether bulk density is quantified or used in a subsequent calculation. Thus, FD-based temporal measurements of soil element mass percentages, elemental mass ratios, and stable isotope composition could also be skewed by concurrent changes in bulk density, but these potential errors are rarely considered in empirical studies.

Our goal is to bring additional attention to the limitations of the FD method and to call upon soil researchers to consider the ESM method not only for evaluating changes in elemental stocks such as SOC, but also for assessing changes in other soil mass-based properties. To this end, we: (a) visually illustrate the potential errors arising with the FD approach when quantifying elemental stocks and other soil properties; (b) demonstrate how the ESM method overcomes FD limitations; (c) compare the errors of the FD method with the errors

of the ESM method; and (d) provide an ESM framework and computer script for researchers to help guide implementation. While we focus our discussion on temporal studies, the same concepts apply to comparative studies that assume identical baseline soil conditions among treatments.

2 | FIXED DEPTH METHOD LIMITATIONS

Changes in soil surface bulk density of 5%–20% are commonly observed following land use change (Bauer & Black, 1981; Don, Schumacher, & Freibauer, 2011) and initiation of management practices including tillage (Dam et al., 2005) and residue addition (Blanco-Canqui, Lal, Post, Izaurralde, & Owens, 2006; Celik, Gunal, Budak, & Akpinar, 2010). When soil bulk density changes through time, the FD approach becomes problematic for quantifying changes in elemental stocks (mass/area) such as SOC because the quantity of mineral soil (mass/area) sampled to an equivalent depth concurrently varies through time (Gifford & Roderick, 2003). This can be demonstrated visually in a hypothetical scenario where 2 cm of compaction at the soil surface causes a 20% increase in soil bulk density from time 0 to time X, while the true SOC stock and mass percentage remain unchanged (Figure 1a). In this case, the soil sampled in the 0–10 cm increment at time 0 has the equivalent mass of the 0–8 cm depth at time X. Thus, the 0–10 cm soil sample taken at time X has 20% more mineral soil mass and subsequently contains 20% more SOC than the 0–10 cm soil sample from time 0. While it is valid to state that there was an increase in the 0–10 cm SOC stock from time 0 to time X, it is incorrect to interpret the SOC change as net C sequestration. In fact, the apparent increase in SOC stock arose entirely from the temporal change in bulk density, as no true change in the profile SOC stock occurred.

In many soils, SOC and N mass percentages vary throughout the soil profile (e.g., Hobley & Wilson, 2016; Lawrence, Harden, Xu, Schulz, & Trumbore, 2015) such that changes in bulk density can lead to errors in FD-based temporal comparisons of those soil properties. For example, in a scenario where SOC mass percent decreases with depth, the soil becomes compacted, and there is no true change in the SOC stock between time 0 and time X (Figure 1b), the SOC mass percentage in the 0–10 cm sampling depth appears to decrease over time. This artifact arises because additional "deep" layers with lower SOC mass percent are sampled at time X, and thus the sampled SOC mass percentage is diluted relative to time 0. Notably, this scenario leads to an apparent increase in the SOC stock despite the apparent decrease in SOC mass percent. Thus, depending on whether changes in SOC mass percentages or SOC stocks are evaluated, it may be concluded that the soil has lost or gained SOC, respectively. In both cases, the conclusions are incorrect, as the true SOC mass percentage and SOC stock remained constant through time, and only the soil bulk density changed.

Ratio-based soil properties such as C:N and δ^{13}C also tend to change throughout the soil profile (e.g., Batjes, 1996; Kramer, Lajtha, & Aufdenkampe, 2017), and therefore their quantification
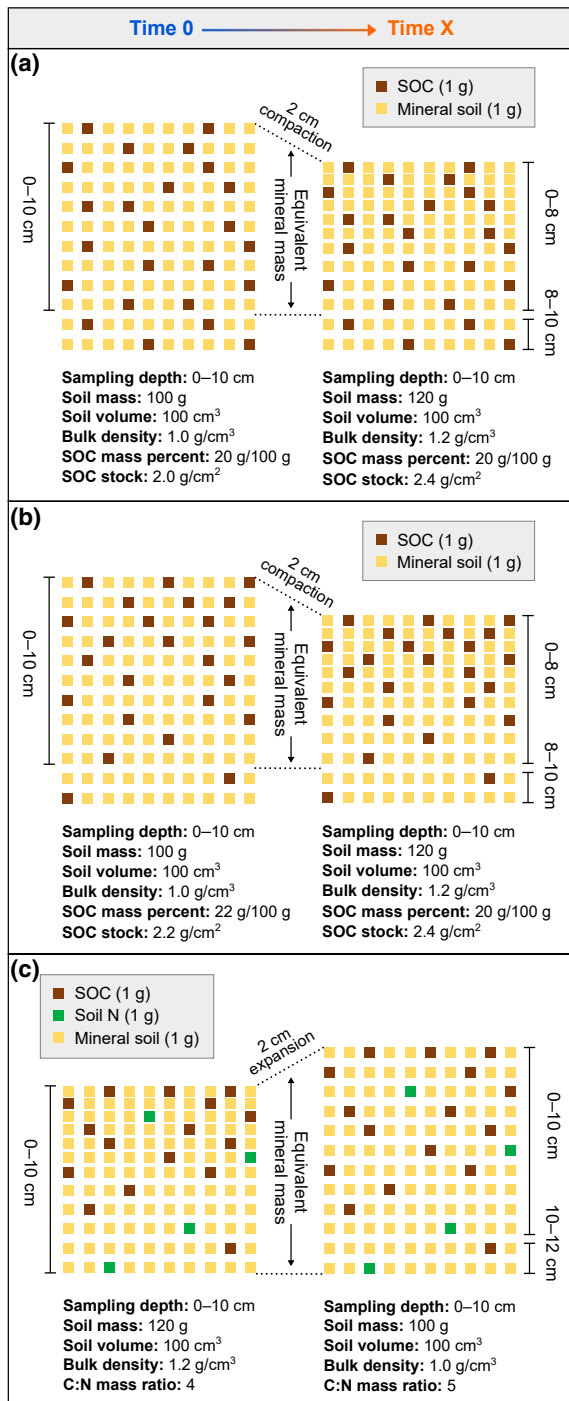
FIGURE 1 Hypothetical scenarios of soil compaction (a, b) or soil expansion (c) from time 0 to time *X*. Each square represents 1 g of soil organic carbon (SOC), mineral soil, or soil N, and the masses are conserved between time 0 and time *X* within each panel. Each soil column is 1 cm from front to back and 10 cm wide, thus the volume for a 10 cm deep sample is 100 cm³. SOC mass percentage remains constant with depth in panel (a) and decreases with depth in panel (b). In panel (c), the soil C:N mass ratio decreases with depth. The illustrations are intended for conceptual purposes only

is also subject to errors with the FD approach when bulk density is altered. For instance, Figure 1c shows a hypothetical soil profile where the soil C:N mass ratio decreases with soil depth. In a
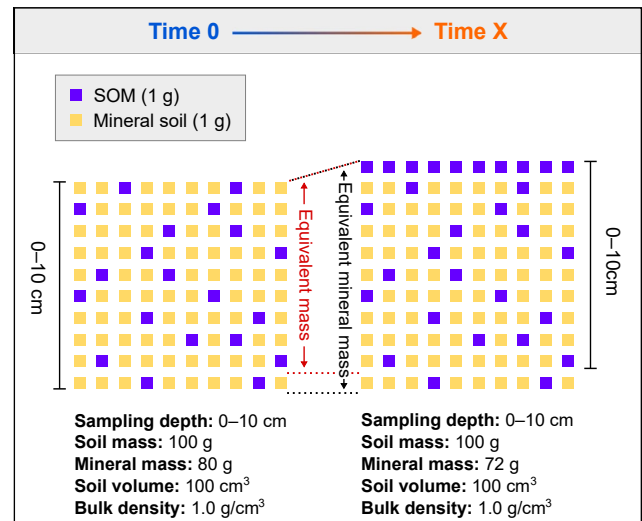

FIGURE 2 A hypothetical scenario where soil organic matter (SOM) is deposited on the surface of a soil column between time 0 and time *X*. Each square represents 1 g of SOM or mineral soil, and the mineral soil is conserved between time 0 and time *X*. The added SOM causes the soil volume to expand, and therefore the 0–10 cm sampling depth at time *X* does not contain the deepest layer of soil

scenario where 2 cm of soil expansion occurs from time 0 to time *X*, the bulk density of the 0–10 cm increment decreases, and the 0–12 cm soil mass at time *X* is equivalent to the 0–10 cm soil mass at time 0. Because the 0–10 cm sample at time *X* does not contain the "deepest," lowest C:N soil layer that was sampled at time 0, the resulting apparent C:N ratio is 20% higher at time *X* than time 0 for the 0–10 cm depth interval. Similar to the previous examples, the apparent temporal increase in soil C:N mass ratio is caused entirely by the bulk density change, as no actual C:N change occurred. While more difficult to demonstrate visually, the same concept applies for stable isotope compositions, which are based on isotope ratios.

When changes in SOM stocks occur, the volume of soil within the profile is likely to change, and therefore FD-based comparisons may be erroneous (Henzell et al., 1967; Skene, 1966). Such errors can occur even if soil bulk density does not change within the sampled FD interval. As a hypothetical example, if SOM is added via aboveground plant biomass turnover at the soil surface between time 0 and time *X*, then the volume of soil expands upward (Figure 2). If bulk density remains constant within the sampling interval, the 0–10 cm sample at time *X* does not account for the "deepest" SOM sampled in the same depth interval at time 0. Consequently, the SOM gain is underestimated by 20%. On the other hand, if SOM was lost from within the time 0 FD interval, the volume of soil would be expected to contract downward. This would cause additional deep SOM to be sampled within the same FD interval at time *X* and thereby underestimate the SOM loss. In both the SOM gain and SOM loss scenarios, changes in SOC and N, which are components of SOM, would be similarly underestimated (e.g., Skene, 1966).

3 | EQUIVALENT SOIL MASS PRINCIPLES

The ESM approach has been presented under many names including spatial mass coordinates (Gifford & Roderick, 2003), cumulative mass coordinates (McGarry & Malafant, 1987), material coordinates (Sposito, Giraldez, & Reginato, 1976), and equivalent depths (Jenkinson, 1971; Powlson & Jenkinson, 1981). Whereas the FD method relies on (cumulative) soil depth as the index for repeated measurements, the ESM approach uses cumulative mineral soil mass per unit area (hereafter referred to as mineral soil mass) as the index. Early ESM implementations required time-consuming operations such as physically sampling to the depth of equal mineral soil mass (Skene, 1967) or mixing soils from adjacent depth increments after sampling (Powlson & Jenkinson, 1981). However, contemporary ESM methods use post hoc model fitting to mathematically adjust measurements to a common mineral soil mass (Rovira, Sauras, Salgado, & Merino, 2015; Wendt & Hauser, 2013).

With the ESM approach, cumulative mineral soil mass serves as a conserved reference between sampling time points (McBratney & Minasny, 2010; Rovira et al., 2015). This concept is similar to the isoquartz method used in some pedogenesis studies, whereby changes in soil mineral and chemical abundances are reported with respect to quartz, which is highly resistant to weathering (e.g., Sohet, Herbautsh, & Gruber, 1988). Cumulative mineral soil mass, which excludes SOM, is a more appropriate ESM index than cumulative total soil mass (Jenkinson, 1971; McBratney & Minasny, 2010; Rovira et al., 2015; Sollins & Gregg, 2017) because SOM stock changes will alter total soil mass but not mineral soil mass (e.g., Figure 2). While the error incurred from using total soil mass as the index is expected to be small in most cases (Rovira et al., 2015), the error will vary as a function of initial SOM stock and magnitude of SOM change (Figure S1).

To compare the FD approach to ESM, consider an example where soil samples containing four depth increments each are taken at time 0 and time X (Figure 3). In this scenario, the soil surface was compacted by 1.5 cm between time 0 and time X, causing an increase in soil bulk density (Figure 3a) but no true changes in other soil properties (Supporting Information). As calculated with the FD approach (Equations A1–A7), the apparent SOC stock within the 0–10 cm interval is greater at time X than at time 0, but the opposite is true within deeper intervals (Figure 3b). When cumulative SOC is plotted against cumulative mineral soil (Equation A12), the time 0 and time X relationships are congruent (Figure 3c), which illustrates that the soil compaction did not affect these relationships. The time 0 cumulative mineral soil masses are selected as the reference masses (shown as vertical gray lines), and the time X cumulative SOC values are interpolated at the reference masses using a cubic spline interpolation model (e.g., Figure 3c inset; Equations A13–A15). Non-cumulative ESM-based SOC stocks are calculated by subtracting the cumulative values between adjacent ESM depth intervals (Figure 3d). The ESM-based SOC stocks are nearly identical between time 0 and time X, which accurately reflects the fact that soil bulk density was the only soil property that changed.
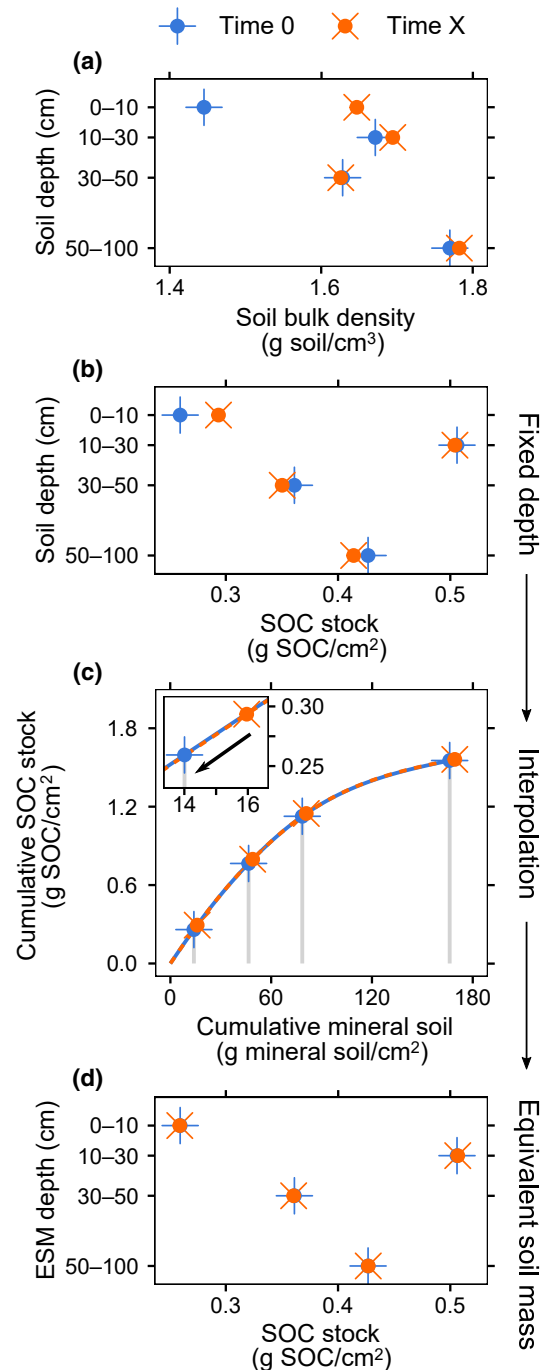

FIGURE 3 Fixed depth (FD) versus equivalent soil mass (ESM) soil organic carbon (SOC) stocks in a scenario where the surface soil was compacted by 1.5 cm between time 0 and time X (a). The time 0 values show the average of empirical values in four bioenergy cropping systems, while the time X values represent simulated soil compaction applied to the time 0 values (Supporting Information). FD-based SOC stocks (b) are converted to cumulative SOC stocks, and cubic spline interpolation models (dashed blue and orange lines) are fit to the cumulative stocks (c). The time X cumulative SOC stocks are interpolated at the time 0 reference mineral soil masses, which are shown as the vertical gray lines (c). The ESM-adjusted cumulative SOC stocks are then converted into non-cumulative form (d). Note that FD values are reported within soil depth intervals (b), whereas ESM values are reported within ESM depth intervals (d)
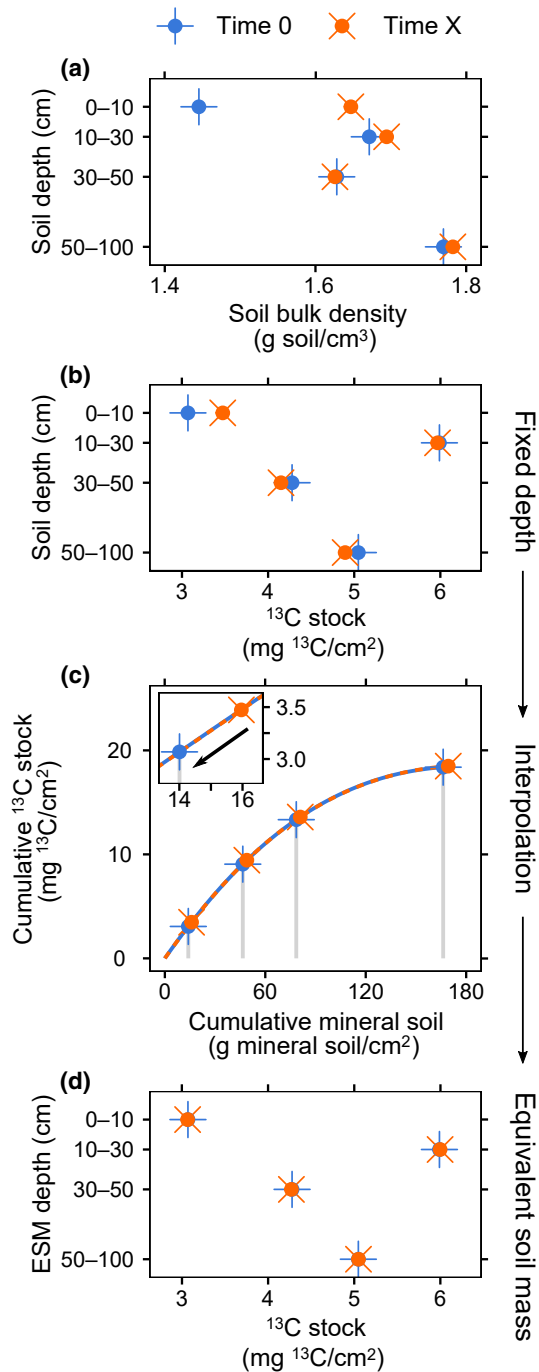
FIGURE 4 Fixed depth (FD) and equivalent soil mass (ESM) ^{13}C stocks in an example where the soil surface is compacted by 1.5 cm between time 0 and time X (a). Time 0 values are the average from four bioenergy cropping systems, and the time X values show simulated soil surface compaction of the time 0 values (Supporting Information). The FD-based ^{13}C stocks (b) are calculated as a function of soil organic carbon (SOC) stocks (Figure 3b) and δ^{13}C values (Figure S2e; Equations A8–A11). Cubic spline interpolation models are fit to cumulative ^{13}C stocks (dashed blue and orange lines), and the time X stocks are interpolated at the time 0 mineral soil masses, which are shown as vertical gray lines (c). Non-cumulative ESM ^{13}C stocks (d) are calculated from the adjusted cumulative ^{13}C stocks. ESM δ^{13}C can be calculated from HSM ^{13}C stocks (d) and ESM SOC stocks (Figure 3d; Equations A8–A11)

By performing ESM adjustments on two soil properties separately, ESM can be used for ratio-based soil properties such as δ^{13}C or C:N. For example, ESM-based δ^{13}C (of SOC) can be derived through separate ESM adjustments of SOC stocks (Figure 3) and ^{13}C stocks (Figure 4). FD-based ^{13}C stocks (Figure 4b) are calculated as a function of the SOC stock (Figure 3b) and δ^{13}C value (Figure S2e; Equations A8–A11), assuming that the relative abundance of ^{14}C is negligible. Interpolation models between cumulative mineral soil and cumulative ^{13}C stocks are fit (Figure 4c; Equation A17), and time X cumulative ^{13}C stocks are interpolated at the time 0 cumulative mineral soil reference values (e.g., Figure 4c inset). Non-cumulative ^{13}C stocks are then tabulated (Figure 4d), and the ESM-based δ^{13}C value are calculated as a function of the ESM-SOC stocks (Figure 3d) and ESM-^{13}C stocks (Figure 4d) within each ESM depth interval (Equations A8–A11). Similarly, for soil C:N mass ratios, ESM-adjustments are performed on SOC and N separately (Equations A15 and A16), and the resulting values are expressed a C:N mass ratio within each ESM depth interval (Figure S3).

To facilitate interpretation, ESM-based soil properties can be reported at "ESM depth" intervals (e.g., Figure 3d) rather than at the mineral soil mass equivalents (e.g., Gifford & Roderick, 2003; Lee et al., 2009). ESM depth intervals refer to the depths at which the reference mineral soil masses occur within the reference samples. For example, the reference cumulative mineral masses in Figure 3 were taken from time 0, and therefore the ESM depths pertain to mineral soil masses contained within each depth interval of the time 0 sample. Because the mineral soil masses from time 0 were used to adjust time X soil properties, the mineral soil stocks at time X are equal to those at time 0 within each ESM depth interval.

A central assumption of ESM is that there is no gain or loss of mineral soil mass between sampling time points (McBratney & Minasny, 2010). For example, if mineral soil is transported laterally from the soil surface via erosion, then mineral soil mass cannot be used as an index because it is not conserved. The FD method suffers similar limitations when soil is lost or gained, and thus this issue represents broader issue for soil-based accounting (Sanderman & Chappell, 2013). On longer timescales, mineral soil mass can be lost via weathering, thus also rendering the mineral soil mass index unsuitable. For this case, other mass- and volume-based indexing approaches have been suggested (Sollins & Gregg, 2017; Zhang et al., 2019).

4 | FD VERSUS ESM ERRORS

The ESM method in principle provides more reliable temporal comparisons than the FD approach, but the ESM procedure is likely to induce some error. Error may arise from the calculation of cumulative stocks (summation of errors) or from inaccuracies in the interpolation procedure, and these errors may be further compounded when multiple ESM adjustments are required (e.g., for ratio-based soil properties). We used a combination of field data and model simulations to compare the potential errors arising from the FD and

ESM methods under altered bulk density scenarios. Briefly, using a soil dataset collected from four bioenergy cropping systems in central Illinois, United States, we applied simulations ranging from 2.5 cm of soil surface expansion to 2.5 cm of compaction to mimic changes in soil bulk density with no true changes in other soil mass-based properties (Figure S2; Supporting Information). We then calculated SOC- and N-related soil properties using both the FD and ESM approaches (Equations A1–A17). We computed errors using the difference between the FD-based soil properties with no bulk density change and the FD- and ESM-based soil properties under the simulated bulk density change scenarios (Supporting Information). The errors were reported as absolute percentage error (%) for mass percentages, stocks, and elemental ratios and as absolute error (‰) for isotope delta values.

When 2.5 cm of surface expansion or compaction was simulated, mean absolute percentage errors for SOC stocks, SOC mass percentage, and C:N mass ratio were 3–102 times greater with FD than with ESM (Table 1). When considering all depth intervals, percentage errors with both methods were highest for SOC stocks, lowest for C:N, and intermediate for SOC mass percent. For SOC stocks, mean absolute percentage error was largest in the 0–10 cm interval with FD, but the percentage error was smallest in that depth interval with ESM. With both methods, mean absolute percentage error increased with depth for SOC mass percent and C:N mass ratios. The mean absolute errors for $\delta^{13}C$ increased with depth for both ESM and FD methods but were three to six times greater with FD (Table 1). Within the 50–100 cm interval, mean absolute errors for $\delta^{13}C$ were at least 0.2‰ greater with FD than ESM.

To investigate how the magnitude of error was affected by varying degrees of bulk density change, we evaluated SOC stock errors across 11 scenarios ranging from 2.5 cm of expansion to 2.5 cm of compaction at 0.5 cm intervals (Figure 5; Supporting Information). Across these scenarios, the mean absolute percentage errors for

SOC stocks increased with degree of expansion or compaction but were consistently lower for ESM than for FD (Figure 5). Within the 0–10 cm depth interval, mean absolute percentage error resulting
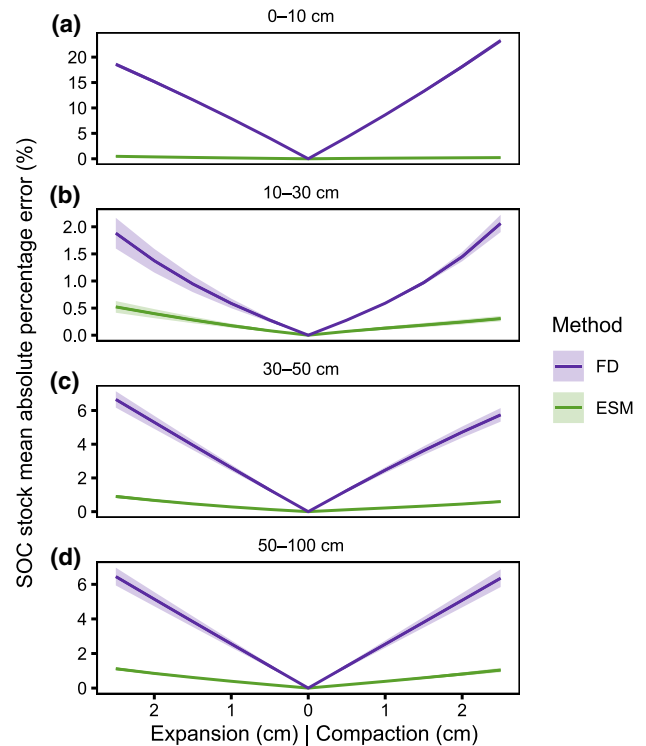

FIGURE 5 Absolute percentage errors resulting from use of the fixed depth (FD) and equivalent soil mass (ESM) methods to calculate soil organic carbon (SOC) stocks across simulations ranging from 2.5 cm of soil surface expansion to 2.5 cm of compaction at 0.5 cm intervals. Panels show 0–10 cm (a), 10–30 cm (b), 30–50 cm (c), 50–100 cm, and (d) depth intervals. Lines give the means while shaded areas show the standard error among four bioenergy cropping systems

TABLE 1 Mean absolute errors incurred from calculating soil soil organic carbon (SOC) stocks, SOC mass percentages (g SOC/100 g soil), soil C:N mass ratios, and $\delta^{13}C$ with equivalent soil mass (ESM) and fixed depth (FD) methods under two scenarios. Soil properties in the two scenarios were simulated by applying 2.5 cm of soil surface compaction or expansion to a baseline scenario, which was derived from empirical measurements in four bioenergy cropping systems (Figure S2; Supporting Information). SOC stocks, ^{13}C stocks, and C:N ratios for the baseline scenario are shown as time 0 in Figures 3 and 4, and Figure S3, respectively

| Scenario	Depth (cm)	Bulk density (g soil/cm³)	Mean absolute percentage error (%)						Mean absolute error (‰)	
			SOC stock		SOC mass percent		C:N ratio		$\delta^{13}C$	
			ESM	FD	ESM	FD	ESM	FD	ESM	FD
Compaction	0–10	1.80	0.2	23.2	0.2	1.4	0.1	0.6	0.011	0.066
	10–30	1.70	0.3	2.1	0.3	3.3	0.1	0.8	0.015	0.091
	30–50	1.63	0.6	5.7	0.6	5.6	0.3	1.3	0.037	0.142
	50–100	1.79	1.0	6.4	1.0	7.0	0.6	2.2	0.129	0.391
Expansion	0–10	1.16	0.5	18.6	0.5	1.7	0.2	0.7	0.022	0.084
	10–30	1.60	0.5	1.9	0.5	2.7	0.2	0.7	0.023	0.069
	30–50	1.64	0.9	6.7	0.9	6.2	0.3	1.4	0.035	0.154
	50–100	1.75	1.1	6.4	1.1	7.3	0.5	2.0	0.099	0.340
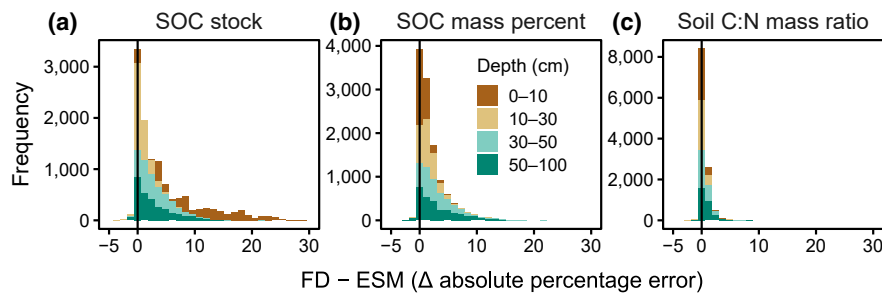
FIGURE 6 The difference (Δ) between fixed depth (FD) and equivalent soil mass (ESM) absolute percentage errors (FD − ESM) when calculated for individual soil samples from bioenergy cropping systems under scenarios ranging from 2.5 cm surface compaction to 2.5 cm expansion at 0.5 cm intervals. Panels show soil organic carbon (SOC) stocks (a), SOC mass percentages (b), and soil C:N mass ratios (c). Bins to the right of zero indicate occurrences of greater error with the FD method, and bins to the left of zero show instances of greater error with the ESM method

from only 0.5 cm of expansion or compaction exceeded 4% with FD, whereas error for the same scenarios was less than 0.1% with ESM. In the 50–100 cm depth interval, 0.5 cm of surface expansion of compaction resulted in absolute percentage errors of approximately 1.25% and 0.2% for FD and ESM, respectively.

When considering all 11 expansion and compaction scenarios applied to each soil sample individually, the FD method consistently produced equal or greater absolute percentage error than ESM for stocks, mass percentages, and mass ratios (Figure 6). The difference between FD and ESM absolute percentage error was greatest for SOC stocks, lowest for C:N mass ratios, and intermediate for SOC mass percentages. Although the simulations indicated that the advantage of ESM over FD was typically greatest when calculating elemental stocks, ESM also often provided a benefit for quantifying soil elemental mass percentages and elemental mass ratios.

5 | ESM IMPLEMENTATION

Soil sampling for ESM is generally performed at depth intervals that are selected to capture the anticipated changes within the soil profile (Wendt & Hauser, 2013) while also providing adequate vertical resolution for interpolation models. Soil samples used for ESM must have a known dry mass and cross-sectional sampling area, multiple depth segments should be sampled, and contiguous adjacent depth increments are required when multiple depths are collected (e.g., 0–10, 10–30, 30–50 cm, etc.). Soil segments that are sampled deeper than a contiguity break cannot be used for ESM because it is not possible to calculate cumulative quantities beyond the break. For this reason, contiguous soil cores taken using a hammer or hydraulic apparatus and separated into multiple segments are ideal for ESM. Dividing the cores into many short increments (e.g., 5 or 10 cm in length) will shorten ESM interpolation distances and thus likely decrease the overall ESM method error (Ellert & Bettany, 1995). In addition, segmenting cores at discrete soil boundaries, such as the interface of soil horizons or other sharp transitions (e.g., Ellert & Bettany, 1995), will also help to reduce ESM interpolation errors near the boundaries. To eliminate the need for extrapolation outside of the measured range, soils can be sampled one increment deeper

than intended comparisons (Gifford & Roderick, 2003; Wendt & Hauser, 2013).

Similar to the FD method, accurate quantification of dry soil mass within each sampled depth increment is critical (Wuest, 2009), as dry soil mass is used directly to calculate stocks. Because ESM uses soil mass per unit area as the index, it is not strictly necessary to compute soil bulk density within each depth increment (Gifford & Roderick, 2003; Wendt & Hauser, 2013). However, considering that soil bulk density is a common metric and can easily be converted to soil mass per unit area if the sampling depth increment is known, we find it convenient to work with soil bulk density values. Apparent soil bulk density is calculated from the dry soil mass and sample volume using appropriate accounting for gravel and plant material (Hobley, Murphy, & Simmons, 2018; Rovira et al., 2015; Throop, Archer, Monger, & Waltman, 2012). We use the term "apparent soil bulk density" because the ESM method does not require that the soil bulk density within the collected samples match the true field soil bulk density. That is, inadvertent soil bulk density errors, such as those resulting from compaction of soil cores during sampling, inconsistencies with core segmenting, or soil bulk density changes within a sampling campaign, will have a negligible effect on ESM-based comparisons (Gifford & Roderick, 2003; Wuest, 2009) because the relationship between cumulative mineral soil mass and other cumulative soil properties will remain intact despite bulk density changes (e.g., Figure 3c). The mitigation of such sampling errors is another significant advantage of ESM that can improve the ability to detect small changes in soil properties, such as SOC stocks (Ellert et al., 2002; Wendt & Hauser, 2013; Wuest, 2009).

Chemical analysis of soil properties (e.g., SOC mass percentage and $\delta^{13}C$) should be performed on the same samples from which dry soil mass is measured and apparent soil bulk density is subsequently calculated (Ellert et al., 2002; Wendt & Hauser, 2013). To provide the ESM index, it is also necessary to determine the mineral soil mass of each dry soil sample. Loss-on-ignition is commonly used to measure mineral soil mass, but the method may not be appropriate for all soil types (Pribyl, 2010). If mineral soil mass data are not available, or if mineral soil mass cannot be adequately determined empirically, then it may be necessary to use an SOC-to-SOM conversion factor such as "Van Bemmelen's factor" of 0.58 g SOC/g SOM (e.g., McBratney & Minasny, 2010; Rovira et al., 2015). If true soil bulk density is of

interest, then more accurate methods to quantify bulk density should be used (Gifford & Roderick, 2003). However, collection of separate samples for true bulk density (e.g., using a short bulk density ring) and other soil properties (e.g., using a long hydraulic corer) is not necessary (Wendt & Hauser, 2013). Moreover, using separate samples for bulk density and other soil properties may result in a mismatch of mineral soil masses within each depth interval between sample types, thus causing errors in calculations such as SOC stocks. We also do not recommend using approximations such as pedo-transfer functions to estimate apparent bulk density for ESM, as these functions commonly result in errors exceeding 10% (De Vos, Meirvenne, Quataert, Deckers, & Muys, 2005), which will propagate into ESM calculations.

It is generally accepted that the specific reference mineral soil mass values used for ESM-based comparisons are not critically important (Ellert & Bettany, 1995; Ellert et al., 2002; Wendt & Hauser, 2013), but there are some practical considerations for selecting the reference masses (Figure S4). If soil samples are collected in a temporally paired design (i.e., from approximately the same location at multiple time points), then the mineral soil mass at the first time point for each location can serve as the reference mass for all subsequent samples taken at that location. When soil samples are collected from random locations within plots at multiple time points, then the reference mineral soil mass can be computed as the average mineral soil mass at the first time point within each plot. In a comparative experiment, the reference mineral soil mass can be calculated as the average mass of samples taken from an appropriate baseline or business as usual treatment. Alternatively, in any type of experimental design, the reference soil masses may be taken from another experiment or protocol (Gifford & Roderick, 2003; Rovira et al., 2015).

Finally, a model fitting procedure is required to adjust depth-based soil properties to the reference mineral soil masses. Linear interpolation (Ellert & Bettany, 1995; McBratney & Minasny, 2010), cubic spline interpolation (Wendt & Hauser, 2013), and non-interpolating models (Rovira et al., 2015) have all been used to make ESM adjustments. Non-interpolating models, such as exponential functions, are unlikely to pass exactly through the points of the original dataset, and therefore they are less accurate for predictive purposes. In addition, non-interpolating functions are less flexible than interpolating models and therefore cannot be expected to provide a good fit for all relationships, particularly when abrupt changes in soil properties occur within the profile. Linear interpolation models will pass through all points of the original dataset, but the linear attribute assumes that soil properties are uniform within each depth increment (Wendt & Hauser, 2013). Considering that many soil mass-based properties change with depth (e.g., Kramer et al., 2017; Lawrence et al., 2015), this assumption is not likely to hold in most situations, and therefore the accuracy may be low for predictions made far from the original data points (Wendt & Hauser, 2013). In cases where several depth intervals are sampled, cubic spline interpolation models can be used (Wendt & Hauser, 2013). Cubic spline interpolation models improve upon linear interpolation models by providing non-linear flexibility between data points while still assuring that the model passes through the original data points. An additional constraint (Hyman, 1983) can be added to preserve monotonic relationships between cumulative soil mass-based properties. In agreement with Wendt and Hauser (2013), we suggest that cubic spline interpolations are preferable for ESM modeling.

6 | SIMPLIFYING ESM CALCULATIONS

To facilitate the adoption of the ESM approach, we developed an R script that uses cubic spline interpolating functions and mineral soil masses to calculate ESM-based SOC stocks and SOC mass percentages (Supporting Information). The script requires the user to input a spreadsheet containing information on upper and lower soil depths (cm), apparent soil bulk density (g soil/cm^3), SOC mass percentage (g SOC/100 g soil), and SOM mass percentage (g SOM/100 g soil) for each soil sample. If SOM mass percentage is not known, then a SOC-to-SOM conversion factor can be used to estimate SOM (McBratney & Minasny, 2010). Each contiguous collection of samples (e.g., one soil core) is assigned an ID, replicate number, and reference ID. These three parameters are used to specify the collection of samples from which the equivalent mineral soil mass is calculated and can accommodate studies that use various experimental designs (e.g., temporal or comparative). Cubic spline interpolation models are fit to each unique instance of ID and replicate (e.g., each soil core), and the reference mineral soil masses for each interval are computed from the samples that contain an ID matching the reference ID. ESM-based SOC stocks and SOC mass percentages are then calculated from the interpolation models and output to a spreadsheet. For comparison, the FD-based calculations are also output to a spreadsheet. While still more burdensome than the FD approach, the R script gives the user the ability to calculate ESM-based SOC stocks and SOC mass percentages for many samples simultaneously.

7 | CONCLUSIONS

Fixed depth-based comparisons of elemental stocks, mass percentages, elemental mass ratios, and stable isotope composition are highly prone to errors caused by changes in soil bulk density or SOM stocks. The ESM method provides consistent improvements across a wide range of bulk density change scenarios, and it is inherently resistant to sampling errors caused by compaction during soil coring or by imprecise cutting during soil sample segmenting. In line with opinions of other authors (e.g., Ellert & Bettany, 1995; McBratney & Minasny, 2010; Wendt & Hauser, 2013), we agree that in mineral soils ESM should be the default method for assessing changes in elemental stocks such as SOC. Moreover, we suggest that ESM may often be the preferred basis for comparisons of soil elemental mass percentages, elemental mass ratios, and stable isotope delta values. We recommend that studies explicitly report and provide details regarding the implementation of ESM.

The use of ESM to quantify changes in soil mass-based properties can enhance our overall understanding of ecosystems and thereby refine predictions of how mineral soils will respond to future changes.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section.

APPENDIX A1

BULK DENSITY AND ELEMENTAL STOCKS

For each soil segment, apparent soil bulk density was calculated as:

$$\rho_{b,soil} = \frac{M_{sample,<2\,mm}}{V_{sample}}, \tag{A1}$$

where $\rho_{b,soil}$ is apparent bulk density of soil < 2 mm (g soil/cm^3), $M_{sample,<2\,mm}$ is the oven-dry mass of soil < 2 mm (g), and V_{sample} is the total volume of the sample (cm^3) calculated from the cross-sectional area of the soil corer (cm^2) and the sampling depth interval (cm). Including the full volume of the soil core but only the mass of soil < 2 mm removes

coarse fractions including gravel and rhizomes from the soil bulk density calculation so that fine earth elemental stocks can be correctly scaled (Throop et al., 2012). For each soil segment

$$M_{soil} = \rho_{b,soil} Z_{segment}, \tag{A2}$$

where M_{soil} is soil mass per unit area (g soil/cm^2) and $Z_{segment}$ is the length of the core segment (cm). Note that M_{soil} can also be calculated as

$$M_{soil} = \frac{M_{sample,<2\,mm}}{A_{sample}}, \tag{A3}$$

where A_{sample} is the cross-sectional area of the soil corer (cm^2). The stock of each element (SOC or N) within each segment was then

$$M_{element} = M_{soil} F_{element}, \tag{A4}$$

where $M_{element}$ is element mass (M_{SOC} or M_N) per unit area (g element/cm^2) and $F_{element}$ is the mass fraction (F_{SOC} or F_N) of the element (g element/g soil). Areal masses of SOM and mineral soil were calculated as

$$M_{SOM} = M_{soil} F_{SOM}, \tag{A5}$$

$$M_{mineral} = M_{soil} - M_{SOM}, \tag{A6}$$

where M_{SOM} is the mass of SOM (g SOM/cm^2), F_{SOM} is the mass fraction of SOM (g SOM/g soil), and $M_{mineral}$ is the mass of mineral soil (g mineral soil/cm^2). Because F_{SOM} was not available for our soil samples, we estimated F_{SOM} following McBratney and Minasny (2010):

$$F_{SOM} = \frac{F_{SOC}}{0.58}. \tag{A7}$$

HEAVY ISOTOPE STOCKS

To express δ^{13}C on an ESM basis, it was first necessary to calculate ^{13}C stocks. Delta values were converted to isotope atom ratios using

$$R_{a,sample} = \left(\frac{\delta_{sample}}{1,000} + 1 \right) R_{a,standard}, \tag{A8}$$

where $R_{a,sample}$ is the sample atom ratio of heavy to light isotopes, δ_{sample} (‰) is the delta value (δ^{13}C) relative to the respective isotope standard, and $R_{a,standard}$ is the atom ratio of heavy to light isotopes in the respective isotope standard (0.0112372 for ^{13}C:^{12}C). The atomic ratios were then converted to mass ratios with

$$R_{m,sample} = R_{a,sample} \frac{A_{heavy}}{A_{light}}, \tag{A9}$$

where $R_{m,sample}$ is the sample heavy-to-light isotope mass ratio, and A_{heavy} and A_{light} are the atomic masses (u) of the heavy and light isotopes, respectively (^{13}C = 13.0034, ^{12}C = 12.0000). Assuming that

other isotope masses are negligible (i.e., ^{14}C), the isotope mass ratio was expressed as mass fraction of the heavy atom.

$$F_{heavy} = \frac{R_{m,sample}}{(R_{m,sample} + 1)}, \tag{A10}$$

where F_{heavy} is the mass fraction of the ^{13}C isotope (g isotope/g element). Heavy isotope stocks were calculated as

$$M_{heavy} = M_{element} F_{heavy}, \tag{A11}$$

where M_{heavy} is the heavy isotope mass (M_{13C}) per unit area (g isotope/cm^2) and $M_{element}$ is the total elemental mass (M_{SOC}) per unit area (g element/cm^2).

CUMULATIVE STOCKS, CUBIC SPLINE INTERPOLATIONS, AND ESM CALCULATIONS

Cumulative stocks were calculated for each segment following McBratney and Minasny (2010):

$$M_n = \sum_{i=1}^{n} M_i, \tag{A12}$$

where M_n is the cumulative stock of $M_{mineral}$, M_{SOM}, $M_{element}$, or M_{heavy} (g/cm^2) at soil layer n, and M_i are the respective non-cumulative stocks in shallower layers (g/cm^2).

Cubic spline models were used to interpolate between cumulative $M_{mineral}$ and cumulative $M_{element}$, M_{heavy}, or M_{SOM} data points. The interpolating cubic spline function is a piecewise polynomial given by Shikin and Plis (1995) as

$$S(x) = S_i(x) = a_0^{(i)} + a_1^{(i)}(x - x_i) + a_2^{(i)}(x - x_i)^2 + a_3^{(i)}(x - x_i)^3, \tag{A13}$$

for each subsegment $[x_i, x_{i+1}], i = 0, 1, \ldots, n - 1$.

The function has continuity $S(x) \in C^2[a, b]$, where $a = x_0 < x_1 \ldots < x_{n-1} < x_n = b$.

The function also meets the conditions $S(x_i) = y_i, i = 0, 1, \ldots, n$.

Interpolating cubic spline models were fit with the 'spline' function in the R 'stats' package (R Core Team, 2019) using the 'hyman' algorithm (Hyman, 1983). The Hyman (1983) algorithm was selected because it preserves the monotonic increase over the range of measured values that is expected between any two cumulative mass variables. The following spline models were fit:

$$M_{SOM} = S(M_{mineral}), \tag{A14}$$

$$M_{SOC} = S(M_{mineral}), \tag{A15}$$

$$M_N = S(M_{mineral}), \tag{A16}$$

$$M_{13C} = S(M_{mineral}), \tag{A17}$$

where all mass values are in the cumulative form, M_n (Equation A12).

The cubic spline interpolation models were then used to make predictions for each variable (M_{SOM}, M_{SOC}, M_N, M_{13C}) at the desired $M_{mineral}$ ESM values. All predicted cumulative masses were subsequently converted to non-cumulative ESM values by subtracting adjacent segments. In each non-cumulative segment, M_{soil} was calculated as the sum of $M_{mineral}$ and M_{SOM}. SOC and N stocks were converted to elemental mass factions by dividing the SOC mass or N mass ($M_{element}$) by M_{soil} within each ESM segment. ESM C:N mass ratios (g SOC/g N) were calculated as the ratio of SOC mass to N mass within each segment. ESM-based SOC stocks and ^{13}C stocks were converted to ESM-$\delta^{13}C$ by reversing Equations A8–A11.