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Diverse Soil Carbon Dynamics Expressed at the Molecular Level

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Abstract

The stability and potential vulnerability of soil organic matter (SOM) to global change remain incompletely understood due to the complex processes involved in its formation and turnover. Here we combine compound-specific radiocarbon analysis with fraction-specific and bulk-level radiocarbon measurements in order to further elucidate controls on SOM dynamics in a temperate and subalpine forested ecosystem. Radiocarbon contents of individual organic compounds isolated from the same soil interval generally exhibit greater variation than those among corresponding operationally defined fractions. Notably, markedly older ages of long-chain plant leaf wax lipids ($n$-alkanoic acids) imply that they reflect a highly stable carbon pool. Furthermore, marked $^{14}$C variations among shorter- and longer-chain $n$-alkanoic acid homologues suggest that they track different SOM pools. Extremes in SOM dynamics thus manifest themselves within a single compound class. This exploratory study highlights the potential of compound-specific radiocarbon analysis for understanding SOM dynamics in ecosystems potentially vulnerable to global change.

Plain Language Summary

Soil carbon forms the largest amount of organic carbon stored on land. In the context of climate change, it is important to know how stable the carbon in this large reservoir is. In this paper we try to attain a better understanding of the stability of soil carbon in a warm and cold area by looking at specific molecules (soil lipids). By measuring the age of these molecules (using radiocarbon) and comparing it to all environmental information, we attain more insight into the soil carbon stability. We found that the molecules show a wide range of ages, indicating they reflect a wide range of sources. These molecular markers may constitute a cleaner method to assess carbon stability than methods that were used previously. They can also indicate the contribution of extremely old (fossil) carbon derived from carbon-holding rocks. Altogether, this paper presents a new approach to tackle soil carbon stability and showcases new insights gained from this approach.

1. Introduction

Soil organic matter (SOM) constitutes the largest terrestrial reservoir of organic carbon (OC), and with ongoing climate and land use change it is essential to attain a better understanding of its stability and dynamics, particularly with respect to the most stable carbon pools (Batjes, 1996; Davidson & Janssens, 2006). However, the inherently complex nature of SOM has confounded attempts to assess potential responses to global change (Doetterl et al., 2015; Schmidt et al., 2011), with timescales of terrestrial carbon turnover remaining one of the largest sources of uncertainty in climate model predictions (Carvalhais et al., 2014; He et al., 2016). Furthermore, while much effort has focused on surface soils, knowledge of the dynamics of the deep soil carbon pool remains particularly elusive despite its key importance in the carbon cycle (Rumpel & Kogel-Knabner, 2011). In order to address and disentangle the complex sources and processes contributing to SOM behavior, operationally defined soil carbon pools are often separated, assuming that they shed light on stabilization mechanisms (Cerli et al., 2012).

The value of combining radiocarbon measurements on bulk SOM and on specific operationally defined fractions for assessment of carbon pools has been previously demonstrated (Schrumpf & Kaiser, 2015). Radiocarbon constitutes a uniquely powerful tool because it allows for the assessment of carbon dynamics on decadal to millennial timescales owing to the bomb spike and natural radioactive decay, respectively.
(Torn et al., 2009). Though fraction-specific data yields improved insights into the dynamics of specific pools as compared to only bulk measurements, it has drawbacks. For instance, in supposedly labile pools (e.g., low density fractions), very stable material (charcoal) can be present (Baisden et al., 2002; Murage et al., 2007). It has been hypothesized that increased temperatures accompanying climate change may lower activation energies necessary for organic matter breakdown (Davidson & Janssens, 2006), promoting destabilization of previously recalcitrant OC. Previous \(^{14}\)C analysis of aliphatic hydrocarbon fractions revealed that these compounds are consistently older than bulk OC, suggesting that they reflect a slowly cycling (passive) carbon pool in soils (Huang et al., 1999). Long-chain \(n\)-alkyl lipids, such as \(C_{26}\), \(n\)-alkanoic acids and \(C_{25}\), \(n\)-alkanes, in soils and aquatic sediments dominated by terrestrial inputs are thought to be exclusively derived from higher plant leaf waxes (Drenzek et al., 2007; Eglinton & Hamilton, 1967; Eglinton et al., 1962; Galy & Eglinton, 2011) and may serve as diagnostic markers for (stable) mineral-bound fractions of SOM due to their hydrophobic characteristics (Lutzow et al., 2006). In contrast, shorter-chain homologues may derive from different biological sources that reside in or trace other SOM pools. For example, short- and medium-chain carboxylic acids \((C_{16}-C_{22})\) may derive from plant, microbial, or root inputs (Reiffarth et al., 2016; Simoneit, 2005). Radiocarbon measurements of soil lipid compound classes by Rethemeyer et al. (2004) have demonstrated the potential of this class of lipid biomarker in identifying SOM source material.

Recent work has illustrated the utility of specific biomarker compounds as indicators of SOM compositional alteration under global change (Feng & Simpson, 2011; Feng et al., 2008), and as tracers of large-scale export of terrestrial organic matter from river drainage basins (Feng et al., 2013; Tao et al., 2015). With the advent of compound-specific radiocarbon analysis (Eglinton et al., 1996), the potential exists to probe SOM dynamics at the molecular level. Overall, there is growing recognition of the potential of biomarkers in soil (carbon) studies (Angst et al., 2017; Jansen & Wiesenberg, 2017), including the insights that can be gained from compound-specific radiocarbon dating (Angst et al., 2016). Furthermore, there is a clear need for an improved understanding of relationships between diagnostic marker compounds and different operationally defined or mathematically modeled SOM pools. In this study, we examine the radiocarbon signatures of lipids (including \(n\)-alkanes and \(n\)-alkanoic (fatty) acids) in soils from two forest ecosystems. The data are assessed within a framework of ancillary information (Etzold et al., 2014; Walthert et al., 2003), including existing and new bulk-and fraction-specific radiocarbon data. We seek to gain a better understanding of carbon dynamics in both top and deep soils, as well as to explore the potential of biomarkers as tracers of specific carbon pools.

2. Methods

2.1. Study Sites and Sampling Methodology

This study focuses on soils from two forested sites (“Lausanne” a temperate Cambisol and “Beatenberg” a subalpine Podzol) that are part of the Long-term Forest Ecosystem Research (LWF) program at the Swiss Federal Institute for Forest, Snow and Landscape Research, WSL (Etzold et al., 2014; Schaub et al., 2011; Walthert et al., 2002). Both soils developed since glacial retreat in this region ~10,000 years ago (Ivy-Ochs et al., 2009). The temperate site has a thin organic layer of 2–3 cm, after which the A horizon extends until approximately 10 cm depth and is followed by the B horizon. The subalpine site has a thick organic layer of around 20 cm, followed by a thin (few centimeters thick) A horizon (Walthert et al., 2003). The temperate site is underlain by a calcareous and shaly moraine, and the subalpine site is underlain by sandstone. With the aim of minimizing the effect of small-scale spatial heterogeneity, 16 soil cores were acquired on a 43 by 43 m (~1,600 m\(^2\)) regular grid (van der Voort et al., 2016). Samples across the grid were averaged to yield a single composite sample based on their bulk density. Compound- and fraction-specific measurements were performed on the upper topsoil (0–5 cm), lower topsoil (10–20 cm), and the deeper soil (60–80 cm) for the temperate site and on the 20–40 cm interval for the subalpine site. Bulk measurements were performed on all depth intervals, extending to 100 and 60 cm depth for the temperate and subalpine sites, respectively.

Dissolved organic carbon (DOC) in soil solution was sampled on a biweekly basis from May to September 2015 at four depths (at 0, 15, 50, and 80 cm below the litter layer, Graf Pannatier et al., 2004, 2011, 2012) with eight lysimeters deployed on the same plot. For details see supporting information (SI) Text S1.1 and Table S1.
2.2. Extraction and Purification of Compounds

The lipids were microwave extracted in closed Teflon vessels using a dichloromethane:methanol (9:1, vol:vol) solvent mixture. Isolation of specific compounds was achieved by preparative capillary gas chromatography as described in Eglinton et al. (1996), Galy et al. (2011), and Tao et al. (2015). Further details regarding the analytical procedures can be found in the SI Text S1.2.

2.3. Density Fractionation

Soil density fractionation was adapted from Cerli et al. (2012). The density fractions obtained designated (i) the free particulate organic matter (fPOM) fraction, the (ii) occluded particulate organic matter (oPOM) fraction, and (iii) the mineral-associated organic matter (MOM) fraction. Concentration of n-alkanes and fatty acids (FA) was measured in each fraction. Procedural details can be found in SI Text S1.3.

2.4. Radiocarbon Analysis and Turnover Time Modeling

Isolated compounds were analyzed as CO2 gas using a gas interface system fitted to a Mini radioCarbon DAting System (MICADAS, Ionplus, Switzerland) at the Laboratory of Ion Beam Physics at ETH Zürich. For 14C analyses of bulk soil samples, density fractions, DOC in soil solution, and the turnover modeling, additional details are given in SI Text S1.4.

3. Results

3.1. Isotopic Signatures of Soil Carbon Pools and Compounds

For both soils, Δ14C values of the isolated compounds (n-alkanoic acids and n-alkanes) exhibit patterns that are distinct from corresponding density fraction-specific DOC, and bulk Δ14C signatures. Overall, the spread in Δ14C values among individual lipid biomarkers increases with depth. Notably, Δ14C variations within n-alkyl lipids are as large or exceed that of the classical fractionation methods. Shorter-chained fatty acids (SCFA) (~C22) consistently have higher Δ14C values than longer-chained fatty acids (LCFA) (~C26). This pattern is reversed in samples carrying a 14C signature on the falling part of the bomb curve (0–5 cm interval in the temperate site). The δ13C values of C16 to C30 FA tend to decrease with increasing chain length (e.g., ~32 to ~41.7‰ at 15 cm depth at the temperate Cambisol) (supporting information (SI) Figure S1), but this correlation (spearman) is only significant at 15 cm depth (SI Figure S1).

At the temperate Cambisol, bulk Δ14C values range from a bomb-enriched signal (~+110‰) in surface soil (2.5 cm) to strongly 14C-depleted (~−250‰) at 90 cm (Figure 1a). From time series radiocarbon data (SI Figure S2) it is known that the 14C label from the bomb peak has decreased in the top 5 cm in the last two decades. DOC Δ14C values are close or exceed present-day atmospheric values. The density fractions show a larger range in Δ14C values than observed in bulk-level data. For example, the fPOM fraction at 2.5 cm is strongly influenced by bomb radiocarbon (~+126‰), whereas the MOM fraction is strongly depleted in Δ14C (~−302‰) at 90 cm. Specific compounds show a much more complex pattern. In the surface (2.5 cm), all lipid biomarkers have a strongly bomb-dominated signature with only the FA C16 having a slightly less 14C-enriched signature. At greater depth, the n-C28 FA and C27 n-alkane clearly exhibit the lowest Δ14C values, while those of the SCFA are more similar to that of DOC. The C27 alkane at 70 cm depth is exceptionally strongly depleted in Δ14C (~−475‰) (Figure 1a).

At the subalpine Podzol, 0–5 cm bulk OM Δ14C values are lower than at the temperate site, and first decrease and then slightly increase with depth (~−17 at 0–5 cm to ~−125‰ at 40–60 cm depth), whereas DOC Δ14C values remain close to or exceed the atmospheric signature even at depth (Figure 1b). From radiocarbon time series analysis it is known that the bomb signal has decreased in the 20 cm thick organic layer during the past ~20 years and that a portion of the bomb radiocarbon signal has propagated into the mineral soil (SI Figure S2). Density fractions also show a larger isotopic spread than the bulk Δ14C, with the fPOM fraction being most 14C-enriched (e.g., 11‰ at 2.5 cm) and oPOM and MOM being the most 14C-depleted fractions at 50 cm (~−176‰ and ~−150‰, respectively). Again, a bimodal distribution of the short-chain versus longer-chain n-alkyl lipids is evident with the former being consistently enriched in 14C (higher Δ14C values). The C29 n-alkane Δ14C values vary relative to that of corresponding LCFA but are consistently more 14C-depleted than equivalent MOM fractions (Figure 1b).
3.2. Abundance and Distribution Lipid Compounds

At the temperate site, the abundance of FA and n-alkanes normalized to total organic carbon (TOC) varies within 1 order of magnitude with depth (Figure 2). With increasing depth, the proportion of SCFA increases at the expense of LCFA (Figure 2a). Both SCFA and LCFA decrease about an order of magnitude from surface to 90 cm (Figures 2a and 2c). The concentration of long-chain (C27–C33) n-alkanes is greatest at the lowest measured depth (90 cm) (Figure 2e). At the subalpine site, the relative abundances for all lipids normalized to TOC remain relatively constant within the soil profiles (Figures 2b, 2d, and 2f).

3.3. Compound Abundance and Turnover Time

Depending on their chain length, individual lipid biomarkers exhibit both shorter and longer turnover times (i.e., higher and lower 14C contents, respectively) than the most stable density fraction (MOM) (Figure 3). The C16 and C22 FA in the deep soil of the temperate site appear to have a markedly faster turnover and are relatively more abundant than corresponding LCFA. The C27 n-alkane in the deep soil exhibits the slowest turnover (~8,500 years). At the subalpine site the SCFA have consistently faster turnover times than the LCFA and the C29 n-alkane. In the deep soil (20–40 cm) turnover times of all measured compounds are on the order of several thousands of years old, while their concentration remains similar to that in the topsoil. The n-alkane average chain length (ACL), an indicator of the dominant vegetation-derived n-alkane homologues, (Collister et al., 1994) in both sites remains similar throughout the profile and is slightly higher at the subalpine topsoil (0–20 cm) (29.6) as compared to the temperate site (27.6). The carbon preference index (CPI), a measure of the contribution of petrogenic (geogenic or reworked) alkanes (CPI = 1) or terrestrial plant (biospheric) alkanes (CPI ≫ 1) (Saliot et al., 1988), in the top 5 cm of the soils of both sites is high (>15), but the temperate site CPI reduces sharply to lower values (~3) (SI Table S2).

3.4. Distribution of Compounds Among Density Fractions

The mass balance reveals that a nonnegligible portion of carbon was lost during the process of density fractionation (≥10%, SI Table S3), which hinders robust quantitative assessments. Nevertheless, with respect to the recovered material, it is evident that the lipids are concentrated in the mineral-associated (MOM) fraction. Shorter-chain FA retain significant association with the aggregate (oPOM) fraction at both sites. At the temperate site, the relative proportion of lipids associated with the MOM fraction increases with depth at the expense of those associated with oPOM fraction and especially fPOM fractions (Figures 4a–4e). Optical microscopy indicates that significant quantities of charcoal are present in both the fPOM and oPOM fractions in topsoil and deep soil from both sites (SI Figure S3).

4. Discussion

4.1. Biomarker Origins and Associations

Schmidt et al. (2011) introduce the concept of the soil carbon recalcitrance as an ecosystem property (i.e., a function of both environmental and biological controls) rather than a function of the chemical structure.
In this framework, it is crucial to consider both the biomarker provenance as well as the physical association. Previous studies have focused on both the provenance of specific n-alkanes and FA as well as their stabilization mechanisms (Feng et al., 2008; Jandl et al., 2004; Lutzow et al., 2006; Simoneit, 2005; Wiesenberg et al., 2012). Jandl et al. (2004) found indications that (C\textsubscript{21–C34}) FA are occluded in macroaggregates. SCFA are suspected to be derived from microbial sources (Diefendorf & Freimuth, 2017) and roots (Wiesenberg et al., 2010), while LCFA in terrestrial sediments and soils are derived from vascular

**Figure 2.** (a and b) Concentration (mg/gOC) of short-chain fatty acids (SCFA) and relative abundance of SCFA to total FA. (c and d) Concentration (mg/gOC) of long-chain fatty acids (LCFA) and relative abundance of LCFA to total FA. (e and f) Concentration of and long-chain n-alkanes (μg/gOC) and pH in the temperate and subalpine site.
Plants (Drenzek et al., 2007; Galy & Eglinton, 2011). Long-chain \(-n\)-alkanes are thought to be exclusively derived from leaf waxes (Eglinton & Hamilton, 1967; Eglinton et al., 1962).

We find that SCFA appear to be relatively abundant in the oPOM as compared to the LCFA (Figure 4), indicating that the SCFA in particular may play an important role in aggregates. Interpretation of the isotopic

Figure 3. Concentration (mg/g organic carbon in bars) and turnover time (years in points) of lipid biomarkers at various depths in (a) temperate and (b) a subalpine site. The black line indicates turnover time of the MOM fraction. Fatty acid is abbreviated to FA, \(n\)-alkanes to \(n\)-alk, and associated numbers refer to the chain length.

Figure 4. Relative abundance of (a and b) short-chain fatty acids (SCFA), (c and d) long-chain fatty acids (LCFA), and (e and f) \(n\)-alkanes in the labile fPOM (green), semilabile oPOM (blue), and stable mineral-associated MOM (black fractions) in the temperate and subalpine site.
signatures of SCFA is confounded by the multitude of potential sources (aboveground plants, roots, and microbes). The C₁₆ and C₁₈ FA can be initially produced by plants, subsequently allocated to the soil through the fine roots, where they may be transported (in dissolved or colloidal form) and recycled by microorganisms (Bull et al., 2000; Matsumoto et al., 2007). The relatively short turnover times of SCFA as compared to the LCFA in the deep soil confirm that the former comprise part of a faster-cycling C pool. However, the deep soil SCFA turnover times are long nonetheless (centennial to millennial), implying a high degree of stabilization (Figure 3), potentially via protection against degradation within soil aggregates (Lutzow et al., 2006). Wiesenberg et al. (2010) obtained data suggesting that the FA C₂₀–C₂₄ homologues could serve as markers of root-derived inputs. However, the lower Δ¹⁴C values and correspondingly long turnover times (Figures 1 and 3) indicate that these FA are not mainly produced by roots as this would require exudation of strongly preaged carbon (>100 years at 10–20 cm) from young (several-year-old) roots (Solly et al., 2013), exceeding typical plant life spans. The LCFA and higher n-alkanes, which are uniquely plant leaf wax derived (Eglinton & Hamilton, 1967; Eglinton et al., 1962; Reiffarth et al., 2016), are generally more ¹⁴C-depleted than the SCFA. The implied higher degree of stabilization and lower susceptibility to degradation is likely due to their hydrophobicity and propensity to associate with mineral phases (Figure 4) (Lutzow et al., 2006). The ACL suggests that the temperate site (C₂₇–C₂₉ dominated) is influenced by deciduous tree species (Zhang et al., 2008), while the subalpine Podzol with pine trees which are known to contribute few alkanes to soils (Schäfer et al., 2016) may be potentially more strongly impacted by forb-derived (C₂₉ dominated) n-alkanes (Bush & Mcinerney, 2013). The δ¹⁳C signature of bulk soil trends toward higher values with increasing depth, attributed to increasing SOM transformation that results in preferential respiration of ¹³C-depleted carbon (Krull & Skjemstad, 2003; Wynn, 2007; Wynn et al., 2005). However, no such isotopic trend is observable within the lipid compound class as a function of depth (SI Figure S1). The ¹³C-depleted nature of complex hydrocarbon lipids is known to reflect isotopic fractionation during their biosynthesis (Diefendorf & Freimuth, 2017), and the range in δ¹³C values found in this study falls within the typical range for C₃ terrestrial plants (Cooper et al., 2015; Hobbie & Werner, 2004). The turnover times or mean residence times of LCFA and n-alkanes in the upper 5 cm of mineral soils observed in this study show a much wider range than the one previously estimated by Schmidt et al. (2011). It is important to note, however, that the estimates reported by Schmidt et al. (2011) were based on ¹³C-labeling experiments, which while widely used (Six & Jastrow, 2002), can yield turnover times that differ sharply from those based on natural abundance ¹⁴C measurements (Feng et al., 2017; Paul et al., 2001).

In deeper soils, estimates of carbon turnover could be confounded by vertical transport of dissolved organic matter, providing an input of younger carbon (Figure 1; Sanderman et al., 2008; Tipping et al., 2011). The long turnover times of plant leaf wax lipids observed in this study clearly imply resistance to decomposition that is likely related either directly or indirectly to their (physico)chemical characteristics.

### 4.2. Controls on Biomarker Turnover Times

The lipid compounds examined in this study equal or exceed the range in Δ¹⁴C values and corresponding turnover times than density fractions from both study locations. In particular, long-chain lipids are notably depleted in ¹⁴C, in most cases more so than corresponding mineral-associated (MOM) fractions, implying slower turnover rates. This suggests that these compounds may serve as more specific tracers of the oldest (slowest) soil carbon end-member, or passive C pool as originally proposed by Huang et al. (1999). In our study, this interpretation is bolstered by direct comparison with density fraction ¹⁴C data, as well as evidence that these long-chain lipids are concentrated in the MOM fraction (Figure 4). Notably, the spread in Δ¹⁴C values among individual compounds increases with depth (Figure 1), despite relatively constant proportions of alkanes and FA throughout the soil profile at the subalpine site (Figure 2). These trends suggest that differences in soil ages may be amplified as a consequence of differential stabilization mechanisms (Figures 1–3). Overall, these general trends confirm the inferred recalcitrance of long-chain n-alkyl lipids (Lutzow et al., 2006), with this resiliency potentially being a consequence of their hydrophobicity and propensity to associate with (and be afforded protection by) mineral surfaces. Furthermore, the marked increase in relative abundance of microbially derived SCFA (Figure 4) in the oPOM as compared to the LCFA coupled with the relatively slow turnover times of SCFA (>100 years below the top 5 cm) (Figure 3) suggests that these compounds are relatively stable, likely through occlusion in aggregates as is supported by recent findings of Angst et al. (2017) (Figure 4). This carbon pool may potentially be vulnerable to environmental changes.
as drought conditions which are projected to occur more frequently (Dai, 2013; Meehl et al., 2007; Spinoni et al., 2015) may induce destabilization of aggregates (Muhr et al., 2010) and expose associated organic matter to microbial attack.

It is notable that $\Delta^{14}C$ values of the long-chain $n$-alkane ($n$-C$_{27}$) are consistently lower than those of corresponding LCFA, except in the upper 5 cm of the soil. The lower $\Delta^{14}C$ values of the $n$-alkane (longer turnover times $>1,000$ years in the deep soil) imply that they reflect a SOM pool that would be largely impervious to environmental changes. One potential explanation for the difference in $\Delta^{14}C$ values between the $n$-alkane and LCFA is that their more hydrophobic nature and the absence of functional groups render the former more resistant to degradation, possibly via closer association with mineral phases (Lutzow et al., 2006). Alternatively, there may be additional nonleaf wax and “younger” sources of LCFA, such as from roots (Wiesenberg et al., 2012) or possibly microbial metabolites (Gong & Hollander, 1999). Finally, it is possible that a portion of the $n$-alkane signature is derived from fossil C inputs of natural or anthropogenic origin. The $n$-alkane turnover time in the temperate deep soil ($\sim 8,500$ years) nears the time of soil formation, indicating that there likely is a strong geogenic or petrogenic contribution of $n$-alkanes, likely from some of the shale in the moraine that underlies the site. The lower CPI value for deep soil $n$-alkanes ($\sim 3$) is consistent with a potential petrogenic influence (Saliot et al., 1988). From isotopic mass balance, assuming the $\Delta^{14}C$ value of petrogenic carbon is $-1,000\%$ and that of the “unpolluted $n$-alkane” to be similar of the C$_{28}$ FA, we infer an approximate petrogenic contribution to the C$_{27}$ $n$-alkane of $\sim 30\%$ (SI Table S4). The incorporation and potential remineralization of geogenic carbon can cause soils to be an additional source rather than sink of carbon (Petsch et al., 2001). Furthermore, such incorporation of petrogenic C into deeper soils can result in an artificially low apparent turnover time of carbon as determined from bulk or fraction-specific $^{14}C$ measurements.

The bimodal trends between SCFA and LCFA combined with their relative concentrations in different operationally defined fractions have ramifications for soil carbon transport in erosional settings. Doetterl et al. (2012, 2016) highlighted the importance and impact of the erosional setting of landscapes, finding an overall higher storage potential in eroding soils owing to redistribution processes. Additionally, fPOM fractions are relatively depleted in areas where soil is eroding and enriched in areas where soil is accumulating, implying that the MOM fraction would be concentrated on eroding slopes (Berhe et al., 2012). Given that LCFA (and long-chain $n$-alkanes) have a relatively high turnover time (Figure 3) and are concentrated in the MOM fraction, the erosional mechanism put forward by Berhe et al. (2012) would likely amplify the long-term storage potential of these compounds and increase their significance as a component of soil carbon exported from catchments and entrained in fluvial networks.

4.3. Biomarkers Versus Operationally Defined Pools

In both this and other investigations (Baisden et al., 2002; Murage et al., 2007), charcoal—considered a relatively recalcitrant carbon phase (Lutzow et al., 2006)—was found in the supposedly labile fractions (fPOM). Furthermore, Kalbitz and Kaiser (2008) and Schrumpf et al. (2013) have indicated that fresh DOC can be incorporated into the supposedly old and stable MOM fraction. This study has revealed that the lipids not only cover the same isotopic range as the operationally defined fractions but also display an even greater spread in $\Delta^{14}C$ values, particularly in the domain of the most stable compounds. Radiocarbon measurements on specific marker compounds serve to obviate the above interferences on fraction-specific data and thus serve as more definitive sentinels for assessing (changes in) SOM pools. Additionally, the greater range in ages holds promise for refining mathematical models of carbon turnover that encompass a broader spectrum of SOM dynamics.

5. Conclusions

Compound-specific $^{14}C$ and $^{13}C$ data, placed within a context of corresponding information on both bulk and operationally defined OM pools, sheds new light on the large diversity in SOM dynamics. Specific conclusions can be summarized as follows:

1. Lipid compounds span a larger range in $\Delta^{14}C$ values and associated turnover times than classically defined density fractions, especially with respect to those reflecting the most recalcitrant (mineral-associated) carbon pools.
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Diefendorf, A. F., & Freimuth, E. J. (2017). Extracting the most from terrestrial plant-derived leaf wax-derived long-chain n-alkyl lipids (n-alkanoic acids and to some extent, n-alkanes) serve as effective tracers of the most stable plant-derived carbon pool, exhibiting Δ13C values that are consistently lower (older) than corresponding MOM fractions. Long-chain n-alkanes may be influenced by petrogenic contributions, suggesting that the latter may contribute to the apparent long turnover times of deep soil OC. The highly resilient nature (slow turnover) of long-chain leaf-derived plant waxes (n-alkanoic acids and n-alkanes) in soils suggests that this pool of OM is relatively insensitive to environmental change. Microbially derived FA, even in deep soils, suggest direct inputs from more recent C sources such as roots or DOC, implying that may be more vulnerable to changing environmental conditions. Isotopic characterization of specific microbial biomarker lipids may yield clearer insights into dynamic soil carbon pools than those defined with the operationally defined IPOM and oPOM fractions, with the latter prone to interference from other more passive pools (e.g., charcoal). The contrasting dynamics observed at the molecular level have implications not only for assessments of vulnerability of SOM to external environmental forcing but also for the characteristics and fate of OM exported laterally through processes of erosion and fluvial transport.


