

F4 (Fig. C1). A two-pool model with a fast-cycling pool ($\tau = 4$ years) and a variably sized slower-cycling pool was generally able to capture these dynamics with RMSE values below 13.8% (Table 2). With increasing activation energy of the thermal fraction, the proportion of fast-cycling carbon decreased (Fig. 3a) and the turnover time of the slow-cycling fraction increased (Fig. 3b).

As an independent first-order check on the reasonableness of C_{org} MRT results for the thermal fractions, the inventory-weighted MRT of the bulk soil was 16.5 years, matching the results of applying a three-pool turnover model to the bulk ^{14}C data, which varied from 11 to 20 years depending on the model structure (Sanderman et al., 2017).

3.3 Py-GC/MS results

A total of 172 individual compounds were identified in one or more samples. Many of these compounds were a minor fraction of only a single sample. When these compounds were classified by source, there were sharp differences in the dominant chemical compound classes released at each pyrolysis temperature (Fig. 4a). Lipids ($42.5 \pm 2.74\%$) and polysaccharides ($42.4 \pm 2.12\%$) were the dominant classes of compounds released at the lowest pyrolysis temperature (330°C). Relative lipid abundance was $< 10\%$ of the pyrolysis products for all higher temperatures and $< 1\%$ relative abundance at the highest pyrolysis temperature (735°C). Polysaccharides ($51.2 \pm 1.68\%$) remained an abundant component of the pyrolysis products at a pyrolysis temperature of 396°C and 444°C (27.4%) but were $< 10\%$ relative abundance at the two highest temperatures. At the fourth temperature level (503°C), N-bearing compounds, proteins, phenols and unknown compounds dominated the chemical signature and were all $\sim 15\%$ – 20% relative abundance. Phenols (31.4%) were the most abundant compound class released at the highest temperature (735°C), while proteins, aromatics and compounds of unknown origin were all $> 15\%$ relative abundance.

We identified 23 individual compounds that averaged more than one 1% relative abundance across all samples (Fig. 4b). These 23 compounds collectively represented from about $\sim 70\%$ to 90% of the total sample relative abundance at the five different temperatures (Table D1). These compounds included three aromatic compounds, one lignin derivative, one lipid, two N-bearing compounds, two phenols, five polysaccharides, five proteins and four compounds that fell into the unknown origin. The most abundant compound was hexadecanoic acid methyl ester (palmitic acid) with a mean relative abundance across all samples of about 10% but composing 42% of F1 (Table D1). The next two most abundant compounds were both phenols and included phenol and 4-methyl phenol, both increasing with increasing temperature, followed by the common polysaccharide pyrolysis product furfural, primarily found in the lower-temperature fractions.

4 Discussion

While this study has only examined one soil under consistent management over four decades, the combined results from the modeling of the incorporation of bomb-spike ^{14}C into thermal fractions and the stepped Py-GC/MS analysis here suggest that evolved gas analyses can be powerful analytical tools for understanding the complexities of SOM cycling. With increasing activation energy, turnover times increased from decades to centuries (Fig. 3), and there was a consistent (i.e., repeatable across time) strong shift in OM chemistry (Fig. 4).

This investigation was partially framed in the context of testing evolved gas analysis as a tool for isolating biologically meaningful fractions of SOM. The results indicate that each of the five thermal fractions contained unique information. Each of the thermal fractions represented pools with a diverse mixture of organic materials with ^{14}C -based turnover times ranging from 10 to 400 years. A wide distribution of activation energy (Fig. A1) was needed to describe each thermal fraction. Additionally, a one-pool turnover model could not represent the dynamics of ^{14}C in all but the most thermally stable fraction (Table 3). This finding of heterogeneity within an isolated fraction also plagues other physical and chemical techniques for isolating carbon fractions (Sanderman et al., 2013; Torn et al., 2013). Here, by combining ^{14}C -based turnover modeling and compound-specific chemical characterization of the thermal fractions, we have found clues as to reasons for the heterogeneity of SOM within these fractions which provide insights into pathways of SOM formation and longer-term stabilization.

At the two lowest-temperature intervals, where the ^{14}C data suggested rapid turnover rates, the polysaccharides comprised $> 40\%$ of the identified compounds. The dominant polysaccharide products at the two lowest temperatures included furfural, 3-furaldehyde and levoglucosenone. Furfural is a pyrolysis product of hexoses and pentoses as well as uronic acids. The hexoses originate from both plant and microbial residues, while the pentoses are primarily microbial in origin. Levoglucosenone is a pyrolysis product of neutral sugars such as glucose, galactose and mannose (Saiz-Jimenez et al., 1979; Saiz-Jimenez and De Leeuw, 1986). These polysaccharides may be part of partially decomposed residues that dominate the light or particulate fractions of SOM or may be part of other soil carbon pools not strongly protected from thermal degradation by association with minerals. Across all thermal fractions, polysaccharide abundance was strongly correlated with the proportion of fast-cycling carbon in that fraction.

Identifiable lignin derivatives (e.g., syringol and guaiacol) were most abundant in the second and third thermal fractions but never constituted more than 10% of either thermal fraction. While the chemical complexity of lignin likely affords some thermal stability, as suggested by the greater activation energy than the thermal fraction dominated by polysaccha-