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Soil organic matter processes: characterization by ^{13}C NMR and ^{14}C measurements

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Abstract

Soil organic matter (SOM) is a central contributor to soil quality as it mediates many of the chemical, physical, and biological processes controlling the capacity of a soil to perform successfully. SOM properties (e.g. C/N ratio, macro-organic matter) have been proposed as diagnostic criteria of overall soil fitness, but their use is hampered by a poor understanding of the basic biochemical principles underlying SOM processes. The objective of this project was to determine the influence of scrub oak (*Quercus dumosa* Nutt.) and Coulter pine (*Pinus coulteri* B. Don) vegetation on decomposition and SOM formation processes in a lysimeter installation constructed in 1936 in the San Gabriel mountains of southern California. Soil samples archived during construction of the installation, and A horizons sampled in 1987, were fractionated according to density and mineral particle size to isolate the water floatable (macro-organic matter), fine silt and clay fractions. Carbon turnover rates were determined on all fractions from AMS ^{14}C measurements. Solid state CPMAS TOSS ^{13}C NMR was used to semiquantitatively characterize the chemical structure of organic matter on fresh litter and soil fractions. For the two soils, there was a progressive decrease in O-alkyl C, and an increase in alkyl and carbonyl C from the litter to the floatable, fine silt and clay fractions. These compositional differences were due to the oxidative degradation of the litter material, with preferential decomposition of the cellulose and hemicellulose entities and selective preservation of recalcitrant waxes and resins. In all soil fractions, turnover rates of carbon were longer for the pine than for the oak lysimeter (up to 10 times longer). Also under pine, there was a gradual increase in turnover rate progressing from the floatable to the clay fraction, and differences in turnover rates among fractions may be explained based on differences in carbon chemistry. In contrast, under oak, rapid carbon turnover for all fractions suggested intense biological activity in this soil. © 2000 Published by Elsevier Science B.V.

Keywords: Carbon; TOSS CPMAS ^{13}C NMR spectroscopy; AMS radiocarbon measurements; Soil fractions; San Dimas experimental forest; Mediterranean-type ecosystems

1. Introduction

Soil organic matter (SOM) mediates many of the chemical, physical, and biological processes controlling the capacity of a soil to perform successfully; as

such, an assessment of SOM properties is critical to defining overall soil quality. In an effort to characterize quality of agricultural soils from Canada, Gregorich et al. (1994) linked three essential functional roles of organic matter (soil structure, nutrient storage, and biological activity) to a minimum set of soil quality indicators (e.g. total soil organic C and N, macro-organic matter, and carbohydrate content). Such a

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framework is a valuable step towards identification of a quality index that correlates with dynamic SOM processes, but it is hampered by major deficiencies. To allow a more effective interpretation of measurable SOM properties as diagnostic criteria of soil quality, there is a need to better understand the fundamental biochemical processes governing the decomposition and formation of organic matter in soils.

The strong association between organic and mineral soil components has long posed a central challenge to the characterization of SOM chemical structure. A traditional approach has been the extraction of organic substances from soil, such as the use of alkaline hydrolysis followed by acidification, to separate the classical humic and fulvic acid fractions. Undesirable features of this method are an incomplete extraction and a potentially extensive alteration of the extracted products (Stevenson, 1994). In that regard, a most propitious advance in SOM research has been the application of cross polarization-magic angle spinning ^{13}C nuclear magnetic resonance (CPMAS ^{13}C NMR) spectroscopy to whole soils, which dismissed the need for chemical extraction. Continuous development in solid-state ^{13}C NMR technology within the last 10–15 years now allows acquisition of well defined spectra, providing detailed chemical characterization of organic matter in soils (e.g. Oades et al., 1987; Baldock et al., 1992; Preston, 1996).

Atmospheric testing of thermonuclear weapons in the 1950s and 1960s produced a spike input of ^{14}C to the atmosphere, which entered terrestrial ecosystems through plants and subsequently enriched SOM with ‘bomb’ ^{14}C (Goh, 1991). This in situ labeling is a powerful tool for determining SOM turnover rates. In particular, the observed incorporation of ‘bomb’ ^{14}C into the soil has been used to differentiate SOM into a series of pools with different turnover rates, ranging from seasonal to millennial (e.g. O’Brien and Stout, 1978; Scharpenseel et al., 1989; Trumbore, 1993). The use of accelerator mass spectrometry (AMS) now allows ^{14}C measurements to be made on very small sample sizes, about 10 000 times smaller than needed for decay counting (Trumbore, 1996).

The objective of this study was to elucidate the mechanisms of SOM formation and cycling at the San Dimas lysimeter installation by combining CPMAS ^{13}C NMR analysis and C isotopic techniques. The lysimeter installation was originally constructed in

1936 by the US Forest Service to compare the influence of various plant species on water use and hydrological balances (Patric, 1961). Past research at San Dimas has examined vegetation influence on morphological development (Graham and Wood, 1991), aggregate stability (Graham et al., 1995), total soil C and N (Ulery et al., 1995; Quideau et al., 1998), mineralogy (Tice et al., 1996), and base cation weathering (Quideau et al., 1996). Here, we took advantage of the strictly controlled environment at the lysimeter installation to contrast the influence of scrub oak (*Quercus dumosa* Nutt.) and Coulter pine (*Pinus coulteri* B. Don) vegetation on SOM processes. Specifically, we aimed to evaluate how changes in C chemistry during decomposition processes could be related to measured SOM turnover rates.

2. Materials and methods

2.1. Study area

The lysimeter installation is located within the San Dimas Experimental Forest in the San Gabriel Mountains, 56 km northeast of Los Angeles. Climate at the SDEF is Mediterranean, with a mean annual temperature of 14.3°C , and a mean annual precipitation of 678 mm (Dunn et al., 1988). Large (5.3 by 5.3 m horizontally and 2.1 m deep) earthen-walled pits (‘lysimeters’) were filled in 1936 with soil material derived on site from the weathering of diorite. To insure homogeneity, the soil material was sieved (<19 mm diameter), and mixed before filling (Colman and Hamilton, 1947). Composite samples of each 7.5 cm incremental soil layer were taken upon filling, and archived in labeled glass jars. Bulk density of the fill material was calculated from the mass of soil added to the pits (Patric, 1961). The lysimeters were planted in 1946 with chamise (*Adenostoma fasciculatum* Hook. and Arn.), hoaryleaf ceanothus (*Ceanothus crassifolius* Torr.), scrub oak, and Coulter pine. Each planting included a single earthen-walled lysimeter, several concrete-lined lysimeters, and buffer strips to eliminate edge effects. In 1960, a wildfire burned the chamise and ceanothus stands to the ground. The oak and pine lysimeters were less affected, with only spotty burning of the litter under oak. Except for some grass cover under the pine, the

lysimeters have remained as virtual monocultures until present. In the summer of 1987, soils were described from pits as reported by Graham and Wood (1991). Differences in earthworm activity corresponding with plant species played a major role in differentiating the soils. Intense earthworm activity under oak had produced a 7-cm thick A horizon composed largely of worm casts; earthworms were absent under pine and the A-horizon was only 1 cm thick (Graham and Wood, 1991).

2.2. Soil sampling and analysis

In 1987, soil A horizons, and in 1994, litter layers, were sampled in triplicate at the oak and pine lysimeters (Graham and Wood, 1991; Quideau et al., 1998). Precise locations disturbed by sampling were carefully noted and are on file with the USDA Pacific Southwest Forest and Range Experiment Station, Riverside, CA. Bulk density was determined using cores (Ulery et al., 1995; Quideau et al., 1996). All soil and litter samples were brought back to the laboratory for drying and weighing. Archived original fill materials corresponding to the A horizon sampling depths were also examined.

Litter samples were dried at 65°C, and ground in a Wiley mill. Soil samples were air-dried, sieved to remove coarse fragments (>2 mm), and fractionated by density and size separation. Soil samples (20 g) were ultrasonically dispersed in water using a Model 550 Sonic dismembrator (Fisher, Pittsburgh, PA) with a 1:10 soil-to-water ratio and a sonification time of 15 min at full power. The sand fraction (>50 µm) was separated by wet sieving (Anderson et al., 1981), and the macro-organic matter (i.e. the floatable fraction) was isolated from the sand fraction by floatation in water. The remaining soil sample was further fractionated using a combination of sedimentation techniques (Genrich and Bremner, 1974) into: coarse and medium silt (5–50 µm); fine silt (2–5 µm); and clay (<2 µm). The floatable, sand, and coarse and medium silt fractions were dried to constant weight at 65°C. The fine silt and clay fractions were flocculated with 1 M KCl, dialyzed against water until free of salt, and freeze-dried. All fractions were analyzed for total C and N by dry combustion.

CPMAS ^{13}C NMR spectroscopy was used to characterize the chemical structure of organic matter in

litter, floatable, fine silt, and clay fractions of the two soils. Powdered samples were packed in a 7.5-mm diameter cylindrical zirconia rotor with Kel-F caps and spun at 3.2 kHz in a Doty Scientific MAS probe. The CPMAS TOSS (total suppression of side bands) ^{13}C NMR spectra were obtained using a Chemagnetics 200 (Varian NMR, Palo Alto, CA) operating at 74.5 MHz. Preliminary work established that spinning side bands made a significant contribution to the CPMAS spectra, particularly in the aromatic region. While this resulted in a reduction of the signal-to-noise ratio, we decided to run TOSS on all the samples (Hagemeyer et al., 1991). Additional preliminary work showed that the observable ^{13}C resonances in the samples did not change intensity as a function of the contact time for cross polarization. We used the contact time corresponding to maximum intensity for all experiments (contact time: 1.5 ms; pulse delay: 0.2 s). The number of scans for the litter samples was 10 000 and for the floatable fractions about 50 000. For the fine silt and clay fractions, it was necessary to run the experiment for up to 24 h (400 000 scans).

Graphite targets for ^{14}C analysis were prepared by combusting 0.5 to 1 mg carbon at 900°C with cupric oxide wire in evacuated, sealed quartz tubes, and purifying the evolved CO_2 cryogenically in a vacuum line. Graphite targets were then obtained by catalytically reducing CO_2 using the method of Vogel et al. (1987), and were analyzed for ^{14}C by accelerator mass spectrometry (AMS) at Lawrence Livermore National Laboratory, CA. Radiocarbon data were expressed as F , the fraction Modern carbon (where Modern is by definition 1950), and $\Delta^{14}\text{C}$, the ‰ deviation from the $^{14}\text{C}/^{12}\text{C}$ ratio of an oxalic acid standard corrected for radioactive decay since 1950. Positive $\Delta^{14}\text{C}$ values reflect incorporation of bomb ^{14}C , while negative values indicate that ^{14}C has had time to undergo radioactive decay. Average precision for the $\Delta^{14}\text{C}$ values is $\pm 7\%$.

3. Results

3.1. C and N distribution with particle size

Results of C distribution with particle size have been described in detail elsewhere (Quideau et al., 1998), and are summarized here. In 1987, total C

Table 1

Total C and N concentrations in the original fill material, litter sampled in 1994, and A horizons sampled in 1987 under pine and oak^a

Sample	C (g kg ⁻¹)	N (g kg ⁻¹)	C (% total soil)	N (% total soil)	C (g m ⁻²)	N (g m ⁻²)
<i>Archived fill material (0–7 cm)</i>						
Fine silt	7.3 (0.1)	0.72 (0.02)	22.5 (0.3)	22.5 (0.4)	57	5.5
Clay	8.7 (0.4)	0.98 (0.02)	41.8 (1.9)	41.8 (0.8)	106	11.8
Whole soil ^b	2.3 (0.1)	0.19 (0.01)	100.0	100.0	253	20.9
<i>Pine (0–1 cm)</i>						
Litter	511 (4)	13.8 (0.5)	–	–	518	14.0
Floatables	341 (8)	16.2 (3.3)	32.2 (6.4)	24.3 (5.2)	55	2.6
Fine silt	41 (6)	3.0 (0.2)	18.1 (2.0)	21.0 (1.5)	31	2.3
Clay	38 (2)	3.4 (0.2)	21.3 (3.1)	30.5 (4.0)	37	3.3
Whole soil ^b	16 (3)	1.0 (0.1)	100.0	100.0	172	10.8
<i>Oak (0–7 cm)</i>						
Litter	448 (16)	10.1 (0.6)	–	–	490	10.9
Floatables	406 (23)	11.9 (0.9)	46.0 (4.5)	26.4 (5.0)	963	28.2
Fine silt	62 (3)	4.3 (0.2)	15.8 (1.2)	21.0 (0.7)	331	23.0
Clay	43 (1)	4.2 (0.1)	14.7 (1.1)	28.1 (2.0)	308	30.1
Whole soil ^b	32 (1)	1.7 (0.1)	100.0	100.0	2093	109.5

^a Standard errors are indicated in parentheses ($n=3-4$).^b <2 mm.

concentration of the A horizon under oak was 32 g kg⁻¹ (± 1), twice as high as C concentration of the A horizon under pine (Table 1). Concentrations were higher for oak than for pine in all size fractions, but the distribution of C between fractions indicated that the higher C concentration in the soil under oak principally arose from a greater SOM content (g m⁻²) in the floatable fraction. By comparison, no floatable fraction was recovered from the archived soil samples, and the majority of C in these samples was associated with the clay fraction. The floatable C fraction corresponds to the macro-organic matter mentioned by Gregorich et al. (1994), a pool of undecomposed or only partially decomposed plant residues which may serve as a readily decomposable substrate for soil micro-organisms. In contrast, C recovered with the fine silt and clay mineral fractions typically includes more decomposed organic materials.

As for C, total N concentration in the A horizons was higher under oak than under pine in the unfractionated soil samples, as well as in the fine silt and clay fractions (Table 1). On the other hand, N concentration was higher for the pine in the floatable fraction as well as in the litter material. As a result of these differences, C/N ratios under oak were much greater than under pine for the litter and the floatable fraction (Fig. 1).

The C/N ratios continued to decrease from the floatable to the fine silt and clay fractions, reaching in these smaller size fractions similar values under the two vegetation types.

3.2. CPMAS TOSS ¹³C NMR analysis

As illustrated in Fig. 2 for the oak litter sample, NMR spectra showed strong resonances at 72 and 105 ppm, characteristics of C-2, C-3, C-5 and C-1 carbons in cellulose and hemicelluloses, with

Fig. 1. C/N ratios in litter and particle-size fractions from A-horizon samples under oak and pine.

Fig. 2. TOSS CPMAS ^{13}C NMR spectrum of an oak litter sample.

shoulders at 65 and 88 ppm corresponding to the C-6 and C-4 carbons (Duncan, 1987). The peak at 21 ppm was assigned to terminal methyl groups, while the peak at 31 ppm was assigned to alkyl C in long polymethylene type structures (i.e. fatty acids, waxes, resins). The peak at 135 ppm corresponded to C-substituted aromatic carbons, while O-substituted aromatic (phenolic) carbons appeared at 147 and 155 ppm (Hatcher, 1987). Finally, carbonyl functional groups appeared around the peak centered at 173 ppm.

Although TOSS CPMAS NMR is not quantitative for ^{13}C in that the peak intensity does not necessarily reflect the amount of the corresponding carbon, it is semiquantitative if run under carefully controlled conditions at constant speed. Spectra were divided into chemical shift regions as follows (Fig. 2): alkyl C (0–45 ppm); O-alkyl C (45–115 ppm); aromatic C (115–165 ppm); and carbonyl C (165–190 ppm). Magnitude of each chemical shift region was measured by cutting and weighing the corresponding area under the curve, and was expressed as percentage of total area (i.e. relative intensity). The compositional differences noted in progressing from the fresh litter to the floatable, fine silt, and clay fractions were comparable for the oak and pine soils (Table 2). The proportion of O-alkyl carbon progressively decreased from the litter to the floatables, fine silt, and clay, while alkyl and carbonyl C increased. These results are consistent with preferential decomposition of the carbohydrates contained in the litter material, while an increase in the carbonyl region is representative of oxidative degradation processes. The accumulation of alkyl C in the fine silt and clay fractions may arise

Table 2

Distribution of C species in litter and particle-size fractions from A-horizon samples under pine and oak

Sample	Alkyl C (% total C)	O-alkyl C (% total C)	Aromatic C (% total C)	Carbonyl C (% total C)
<i>Pine</i>				
Litter	10.4	69.0	16.1	4.5
Floatables	21.0	46.6	21.6	10.8
Fine Silt	34.4	33.5	14.6	17.5
Clay	39.4	32.9	9.2	18.4
<i>Oak</i>				
Litter	9.7	62.7	20.1	7.6
Floatables	12.6	58.1	20.1	9.2
Fine Silt	23.9	42.1	18.5	15.4
Clay	32.3	35.1	12.1	20.5

either from the selective preservation of recalcitrant litter materials, or from microbial synthesis of new alkyl-type products (Baldock et al., 1992).

While general compositional changes were similar for the two vegetation types, differences were apparent in the magnitude of the changes for the different C species (Table 2). In particular, the decrease in O-alkyl C observed in the floatable and fine silt fractions as compared to the litter was more pronounced under pine than under oak, suggesting a greater decomposition of the cellulose and hemicelluloses contained in the pine litter. This was particularly evident when comparing the litter and floatable fraction. While O-alkyl C made up a greater percentage of total C for the pine litter than was the case for the oak litter, the opposite was true for the floatable fraction. Also, the increase in alkyl C observed in the soil fractions as compared to the litter was greater under pine than under oak.

3.3. SOM turnover rates

The ^{14}C values for the archived and A-horizon samples are presented in Table 3. Negative values for the archived soil fractions reflect the radioactive decay of ^{14}C . The mean residence time (MRT) for carbon present in the original fill material was estimated using the following equation (Trumbore, 1996):

$$\text{MRT} = -\left(\frac{1}{\lambda}\right) \times \ln(F) \quad (1)$$

where F is the fraction Modern carbon, and λ the rate

Table 3
 ^{14}C content, decomposition constant (k), and mean residence time (MRT) for carbon in particle-size fractions from the original fill material and A-horizon samples under pine and oak

Sample	$\Delta^{14}\text{C}$ (‰)	k (per year)	MRT (year)
<i>Archived fill material</i>			
Fine silt	-186.9	0.0005	1660
Clay	-15.0	0.0127	78
Whole soil (<2 mm)	-231.7	0.0040	2130
<i>Pine</i>			
Floatables	220.3	0.0221	45
Fine silt	108.2	0.0149	67
Clay	115.3	0.0128	78
Whole soil (<2 mm)	89.5	0.0126	80
<i>Oak</i>			
Floatables	319.2	0.1155	9
Fine silt	274.2	0.0554	18
Clay	225.4	0.1301	8
Whole soil (<2 mm)	259.4	0.1071	9

constant for the radioactive decay of ^{14}C ($\lambda=0.000121$ per year). The fraction Modern carbon was calculated from the ^{14}C value corrected for the radioactive decay of the oxalate standard since 1950:

$$F = (1.0057 \times 10^{-3} \times ^{14}\text{C}) + 1.0057 \quad (2)$$

This yielded a mean MRT of 2130 years for the fill material carbon (Table 3). Carbon associated with the fine silt fraction was relatively old, suggesting no or little recent carbon input to this fraction. The younger age for the clay-sized C, on the other hand, indicated more recent C input, possibly from dissolved organic carbon in percolating waters, or as a result of SOM mineralization processes in larger size fractions.

The 1987 soil samples and associated soil fractions reflected the incorporation of ‘bomb’ C, as indicated by positive ^{14}C values. A model was developed to simulate carbon fluxes into the soil and decomposition losses. For any given year u , total carbon present in each soil fraction, $C_{t,u}$, was separated into carbon added to the lysimeter soils since planting in 1946, $C_{n,u}$, and carbon still present from the original fill material, $C_{a,u}$:

$$C_{t,u} = C_{n,u} + C_{a,u} \quad (3)$$

with $C_{a,u}$ further defined by

$$C_{a,u} = C_{a,1946} \times e^{-[k_0(u-1946)]} \quad (4)$$

where $C_{a,1946}$ is the amount of carbon originally present in the fill material, and k_0 its decomposition constant, which is equal to $1/\text{MRT}$ as defined in Eq. (1) (Table 3). The increase in C_n with time was fitted to measured carbon contents in the soil using

$$\frac{dC_n}{dt} = b \left[1 - \left(\frac{C_n}{C_{n,1987}} \right) \right] C_n \quad (5)$$

where $b=0.52$ for the pine lysimeter, and 0.275 for the oak lysimeter. Finally, the total ^{14}C content of SOM, $^{14}C_{t,u}$, was obtained using

$$^{14}C_{t,u} \times C_{t,u} = (^{14}C_a \times C_{a,u}) + (^{14}C_{n,u} \times C_{n,u}) \quad (6)$$

where $C_{n,u}$ can be calculated as the following sum for all years over the 1946- u time interval (i.e. x varies from 1947 to year u):

$$^{14}C_{n,u} = \sum I_x \times ^{14}\text{C} \times e^{-[(k_n+\lambda)(u-x)]} \quad (7)$$

with I_x equal to the input of carbon to the soil for year x , and ^{14}C equal to average ^{14}C activity of atmospheric CO_2 for the previous year ($x-1$). The decomposition constants corresponding to the carbon added to the lysimeters between 1946 and 1987, k_n , were then obtained by fitting Eq. (7) for the measured ^{14}C values in the different fractions from the 1987 soil samples. Finally, decomposition constants corresponding to the total C present in each soil fraction, k , were calculated as

$$k = \frac{(C_{n,1987} \times k_n) + (C_{a,1987} \times k_0)}{C_{n,1987} + C_{a,1987}} \quad (8)$$

Changes in ^{14}C content with time for total C in the oak and pine lysimeters are plotted in Fig. 3, and calculated decomposition constants for each fraction are presented in Table 3. Under pine vegetation, $^{14}C_t$ increased at a relatively slow rate with time, reflecting dilution of the $^{14}C_n$ signal by the fill material carbon (Fig. 3). The rate of increase was much greater under oak, since proportionally more new carbon was being added to this soil. Also, $^{14}C_t$ for the oak lysimeter showed a decrease after 1974, which may be related to the decrease in ^{14}C concentration for atmospheric CO_2 after 1965. A lag response of 9 years corresponds to the MRT calculated for total C in the soil under oak (Table 3). In contrast, no decrease in ^{14}C was apparent for the soil under pine over the course of the lysimeter history, as total C in this soil was calculated to have a turnover time of 80 years.

Fig. 3. $\Delta^{14}\text{C}$ content in atmospheric CO_2 and in SOM under oak and pine between 1946 and 1987.

4. Discussion

Results from our NMR analyses, such as the observed decrease in O-alkyl from the litter to the macro-organic matter (i.e. the floatable fraction) to the more decomposed organic materials associated with the mineral soil fractions, are in general agreement with changes noted in other studies where ^{13}C NMR was used to characterize decomposition processes (Oades et al., 1987; Preston et al., 1989; Guggenberger et al., 1995). In particular, Baldock et al. (1992) used NMR to analyze SOM from three different orders (Mollisol, Oxisol, and Andosol), and formulated a model describing the chemical changes associated with organic matter decomposition processes. They proposed that the extent of decomposition followed a continuum from the litter to the soil clay fraction. During the initial stage of decomposition, labile structures, such as cellulose and hemicelluloses, are preferentially degraded by the microbial community, resulting in a decrease of the O-alkyl C signal. At that time, there is an increase in the aromatic C signal due to the selective preservation of these more recalcitrant organic compounds (e.g. lignins). Once the O-alkyl C contained in the original litter materials has been degraded, the second stage of decomposition is initiated; aromatic C is decomposed, and a decrease in the aromatic C NMR signal is observed. The third and final stage of decomposition is characterized by the accumulation of alkyl C (Baldock et al., 1992).

a) Aromatic/ O-alkyl C

b) Alkyl/ O-alkyl C

Fig. 4. Aromatic/O-alkyl C and alkyl/O-alkyl C ratios in litter and particle-size fractions from A-horizon samples under oak and pine vegetation.

Based on the Baldock et al. (1992) model, we considered the applicability of using the aromatic/O-alkyl C ratio as an indicator of the first and second stages of decomposition (Fig. 4a). Under both oak and pine vegetation, the floatable fraction exhibited a higher aromatic/O-alkyl C ratio than the corresponding litter, which is consistent with a preferential degradation of O-alkyl C as compared to aromatic C. The increase in the aromatic/O-alkyl C ratio was more pronounced for the pine than for the oak lysimeter. In a similar fashion, the decrease in C/N ratio between litter and floatable fraction was larger under pine than under oak (Fig. 1). Past work at the lysimeter installation reported intense earthworm activity under the oak vegetation, while earthworms were absent under pine (Graham and Wood, 1991). These earthworm species are endogeic; they live within the soil profile but feed on surface organic matter, such as leaf litter, and may contribute to the mixing of fresh plant residues and mineral soil. In contrast, the litter layer

under pine was composed of three distinct horizons: an Oi1 of fresh pine needles, an Oi2 with partially decomposed pine needles, and an Oe of mostly decomposed needles (Graham and Wood, 1991). The C/N ratios of these horizons decreased from 72.5 for Oi1, to 46.6 for Oi2, to 30.3 for Oe, suggesting progressive decomposition with increasing depth within this litter profile. Based on these results, we conclude that the pine litter material had undergone further decomposition than the oak litter at the time of incorporation into the mineral soil.

The fate of plant residues after their incorporation into the mineral soil was followed by examining chemical changes from the floatable to the fine silt and clay fractions (final products of the decomposition processes). Under pine, the aromatic/O-alkyl C ratio exhibited a small decrease in the fine silt fraction as compared to the floatables, and a further decrease in the clay fraction (Fig. 4a). These changes would correspond to the second stage of SOM decomposition as formulated by Baldock et al. (1992). Under oak, the aromatic/O-alkyl C ratio continued to increase between the floatable and fine silt fraction, and only showed a decrease in the clay fraction. These results suggest that the second stage was attained sooner in the decomposition sequence under pine (i.e. in the fine silt fraction), than it was under oak (i.e. in the clay fraction).

In addition to the use of the aromatic/O-alkyl C ratio, the alkyl/O-alkyl C ratio has also been proposed as an index of the extent of organic matter decomposition in forest soils (Baldock and Preston, 1995). For the two lysimeter soils, the alkyl/O-alkyl C ratio progressively increased from the litter to the floatable, fine silt and, finally, clay fraction, which is consistent with an increase in the degree of decomposition (Fig. 4b). While the alkyl/O-alkyl C ratio was similar for the oak and pine litter materials, this ratio was consistently higher under pine than under oak for the soil fractions. Again, this is in agreement with a higher degree of decomposition for SOM present in the soil under pine.

Results from the ^{14}C analyses indicated in all soil fractions longer SOM turnover rates under pine than under oak vegetation (Table 3). Turnover rate of carbon in soils may be influenced by different factors: (1) the chemical structure of the organic fraction; (2) the nature and activity of the soil biota; and (3) the

interaction between organic materials and the mineral matrix, such as the formation of organo-mineral complexes that are typically more resistant to microbial attack than uncomplexed organic materials. Since the lysimeter installation was constructed from homogenized soil material, we can safely assume that differences between the oak and pine SOM turnover rates were due to differences in the organic fraction of the soils and/or in biological activity. For the pine, the MRT of organic C increased from the floatable to the fine silt and clay fraction. This increase in MRT corresponded to an increase in the alkyl/O-alkyl C ratio, and may be explained on the basis of the extent to which plant residues have been processed by the decomposer community. In progressing from the floatable to the clay fraction, there was a gradual increase in the degradation of the original litter material. This, in turns, resulted in a progressive SOM stabilization within the soil matrix, as indicated by longer MRTs in the finer soil fractions. Under pine, the alkyl/O-alkyl C ratio thus appears to be a good index of the degree of SOM decomposition and of its susceptibility to further microbial attack.

In contrast to SOM present under pine, MRTs of soil carbon under oak did not show clear differences between fractions, nor did they correlate well with the alkyl/O-alkyl C ratios (Table 3 and Fig. 4b). While the alkyl/O-alkyl C ratio increased from the fine silt to the clay fraction, estimated MRT was faster for clay-sized SOM than for SOM associated with the fine silt fraction. As plant materials are incorporated into the mineral soil, they either undergo oxidation to CO_2 , or they are humified to increasingly resistant organic substances. It appears that intense biological activity in the oak lysimeter (i.e. as indicated by very fast C turnover rates in all soil fractions) resulted in rapid SOM oxidation to CO_2 . In turn, this did not allow for the accumulation of SOM with a high degree of humification (i.e. as indicated by NMR results).

Taken together, our results illustrate the importance of combining several experimental approaches, such as NMR and isotopic analyses, to characterize the processes of SOM formation and retention in soils. Under pine vegetation, SOM turnover rates can be explained based on changes in SOM chemistry along the decomposition sequence from the fresh litter to the clay fraction. In contrast, turnover rates of carbon in the soil under oak may be better explained based

on biological activity than on differences in SOM chemistry.

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