# Biological and Molecular Structure Analyses of the Controls on Soil Organic Matter Dynamics

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## 1. INTRODUCTION

The dynamics of soil organic carbon (SOC) are controlled by the interaction of biological, physical, and chemical parameters. These are best measured by a combination of techniques such as long-term field sites with a  $C_3 \leftrightarrow C_4$  plant switch. Acid hydrolysis and  $^{14}\text{C}$ - dating measure the mean residence time (MRT) of the resistant fraction. Long-term incubation allows the *in situ* biota to identify and decompose the labile SOC components. Statistical analysis (curve fitting) of the  $CO_2$  release curves, determines the pool size and of the two labile fractions (1). The effect of chemical structure is measured with pyrolysis-molecular beam mass spectrometry (py-MBMS). The dynamics of charcoal, clay and silt are measured with both  $^{13}\text{C}$  and  $^{14}\text{C}$ .

## 2. MATERIALS AND METHODS

We determined SOC dynamics on continuous maize plots on formerly forested soils, in Ohio and Michigan and a Colorado, grassland loam site. Studies on the Colorado, grassland soils in a wheat-fallow rotation used <sup>13</sup>C and <sup>14</sup>C and acid hydrolysis to characterize the non-hydrolysable C (NHC) and incubation and <sup>13</sup>C to investigate the contribution of the microbial biomass (2, 3). Methodology for the laboratory incubations, fractionation procedures, and tracer analysis are reported by Follett et al. (2), Paul et al. (4), and Collins et al. (5). Methodology for Py-MBMS analyses are reported by Magrini et al. (6).

# 3. RESULTS AND DISCUSSION

The wetland forest in Ohio had an original SOC content of 75 g C kg<sup>-1</sup> soil. Drainage and cultivation dropped this to 18 g C kg<sup>-1</sup> with a MRT of 920 ± 53 yr in the 0-20 cm layer

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and  $6607 \pm 79$  yr at 50-100 cm. Acid hydrolysis that removed ~ 45% of the SOC resulted in an MRT of  $1770 \pm 70$ yr at the surface and  $9875 \pm 75$  yr at lower depths (4)). Continuous maize for 30 yr labeled 21% of the soil  $^{13}$ C. The  $C_3$  (non-maize) SOC had an MRT of 17 yr for the light fraction (LF), 38 yr for the particulate organic matter (POM), 139 yr for the silt, and 261 yr for the clay (Table 1). Incubation for 850 days and measurement of  $^{13}$ C showed the  $C_4$ -C (maize) LF to have an MRT of 3.7 yr, while the plant residues and microbial biomass C within the aggregates (POM) dated 7.8 yr. The maize C in the silt had an MRT of 12.8 yr. The SOC associated with clay was oldest at 26.8 yr.

The Michigan site contained 18 g C kg<sup>-1</sup> soil in the deciduous forest, but 10 g C kg<sup>-1</sup> in the cultivated. The 0-20 cm depth of the cultivated soil had a  $^{14}$ C MRT of 422 ± 50 yr and 1712 yr at 50-100 cm. The non-hydrolyzable C (NHC) accounting for 45% of the SOC had an MRT of 977 yr at the surface, and 4406 yr at depth. The  $^{13}$ C measurements show that in both soils, the LF and POM fractions contain considerable, non-maize C in spite of an extensive period of maize production at both sites. The clay fraction contained the largest portion of the SOC. Both the silt and the clay had much slower  $^{13}$ C turnover rates in the OH soils than in the MI soil (7). This reflects differences for these soils also measured by  $^{14}$ C dating. The Colorado soil lost 33% of its SOC during an 853 day incubation (2) relative to the ~20% loss from the forest-derived sites (5). It had  $^{13}$ C MRTs similar to the OH site, but its  $^{14}$ C dates were much older. The microbial biomass carbon (MBC) was comprised of a labile and stable fraction. The high, initial CO<sub>2</sub> evolution is reflected in the low MRT of the active fraction (C<sub>a</sub>). The NHC comprising 60% of the soil still lost 30% of its C during the 853-day incubation with an increase in MRT from 3175 yr to 4967 yr. There is microbial production and transfers of materials between pools.

The availability of py-MBMS, that rapidly measures volatile pyrolysis products, allows the determination of the molecular structure of the SOC (6). The NHC, although containing a significant proportion of long-chain alkanes and high molecular weight aromatics still contained proteinaceous and carbohydrate materials protected by the soil matrix during hydrolysis. Acid hydrolysis, in removing some of the interfering minerals, results in higher pyrolysis product recovery (8). Interfering materials can also be eliminated by separation of humic acids under an  $N_2$  atmosphere.

Our use of py-MBMS is shown for a cultivated, Colorado Grassland soil before and after an 853 dy incubation (Figure 1). The positive values for the ion intensity represent m/z species present in higher concentrations at day zero than after 853 days. Peaks for amino acids dropped significantly and show the source of some of the 58% of the soil N that was mineralized relative to the 33% of the soil C lost during incubation. The peaks

representing carbohydrates and lignin also dropped during the incubation reflecting the drop in both  $C_3$  and  $C_4$  constituents of the LF and POM during incubation (Tables 1 and 2). Our work has shown microbial production and transfers of materials between pools.

Table 1. Distribution of  $C_4$  and  $C_3$  -C and MRT of the LF, POM, silt and clay fractions of two originally forested soils now in continuous maize

	LF		POM		Silt		Clay		Total
	Ohio silty clay loam								
	C gkg <sup>-1</sup>	MRT yr	C gkg <sup>-1</sup>	MRT yr	C gkg <sup>-1</sup>	MRT yr	C gkg <sup>-1</sup>	MRT yr	C gkg <sup>-1</sup>
C <sub>4</sub> - C	0.6	3.7	1.2	7.8	0.9	13	1.1	27	3.8
C 3-C	0.1	17	0.9	38	3.5	138	9.0	261	13.5
Michigan loam									
C <sub>4</sub> - C	0.3	3.9	0.84	11	0.2	11	1.1	16	2.3
C 3-C	0.2	20	1.4	33	0.9	47	4.2	40	6.7

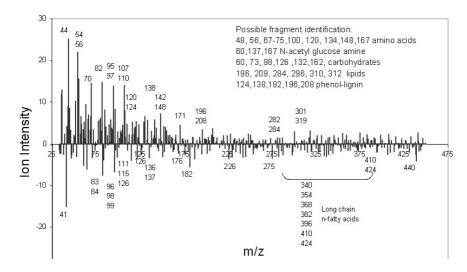


Figure 1. Py-MBMS difference spectrum for a cultivated Colorado grassland (0 day incubation - 853 days). Negative values show species present in higher concentration after 853 days of incubation, positive values show species present in higher amounts at 0 days.

Table 2. The dynamics of analytically-determined fractions of a Colorado silt loam as determined by acid hydrolysis, incubation and <sup>14</sup>C and <sup>13</sup>C measurements

Fraction		Method of Analysis	C, gkg <sup>-1</sup>	MRT, yr
	MBC labile	Incubation – Fumigation	0.18	0.19
	MBC stable	Incubation – Fumigation	0.19	4.6
	C <sub>a</sub> -SOC	Incubation – CO <sub>2</sub> evolution	0.5	0.67
	C <sub>s</sub> -SOC	Incubation - CO <sub>2</sub> evolution	3.2	24
	C <sub>r</sub> -SOC	Acid hydrolysis – 14C dating	5.4	3175
	Total SOC	<sup>14</sup> C dating	9.1	1072
	<sup>13</sup> C from wheat	Incubation – <sup>13</sup> C	4.9	7.5
	<sup>13</sup> C from native	Field – <sup>13</sup> C	4.2	41
	M cr	Incubation-acid hyd- 14C	3.7	4967

MBC = microbial biomass C, Ca = active SOC, Cs = slow C, Cr = resistant C, Mcr = microbial resistant, nonhydrolyzable C

### 4. CONCLUSIONS

A combination of biological analysis, such as incubation and microbial biomass determination,  $^{13}\text{C}$  and  $^{14}\text{C}$  tracers, soil fractionation, and matrix analysis (LF, POM, silt, and clay) with molecular structure analysis (py-MBMS) on long-term sites with a  $C_3 \leftrightarrow C_4$  crop switch provided the tools for determining the interacting controls in SOC dynamics. Mean residence times vary from a few months to 4967 yr. Long-term incubation, in which the soil microbiota decomposed 33% of the SOC and 58% of its N, produced microbial metabolites and transferred materials between pools.

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