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Dynamics of resistant soil carbon of Midwestern agricultural soils measured by naturally occurring ^{14}C abundance

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Abstract

Information on the mean residence time (MRT) of soil organic carbon (SOC) on different soil types and management regimes is required for pedo-geological, agronomic, ecological and global change interpretations. This is best determined by carbon dating the total soil together with acid hydrolysis and carbon dating of the non-hydrolyzable residue (NHC). Midwestern US soils in a transect from Lamberton, MN to Kutztown, PA were found to contain from 33% to 65% of their SOC in the non-hydrolyzable fraction. Soils on lacustrine deposits had the most NHC; glacial till and shale soils, the least. The MRTs of the SOC of surface horizons of soil ranged from modern to 1100 years with an average of 560 years. The MRT increased to an average of 1700 years in the 25–50-cm depth increment and 2757 years at 50–100 cm. The NHC was 1340 years greater at the surface and 5584 years at depth. The MRTs of the total SOC were inversely correlated to sand and directly related to clay content. Silt did not have a significant effect on the MRT of total SOC, but was significantly correlated with the MRT of the NHC. A four-parameter model described the relationship between the SOC content and MRT. The complexity of this equation reflected the strong effect of depth, which greatly decreased SOC while increasing the MRT. The MRT of these soils, as determined with carbon dating of the naturally occurring ^{14}C , was compared to that measured with the ^{13}C signal produced by approximately 30 years of continuous corn (*Zea mays* L.) (C_4) on soils with a known plant history of C_3 – C_4 cropping. The equation of ^{14}C MRT = $176(^{13}\text{C MRT})^{0.54}$ with an R^2 of 0.70 showed that although short-term ^{13}C studies correlate well with the total MRT, they reflect the dynamics of the active and slow pools, not the total SOC. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: ^{14}C ; Carbon dating; Soil organic carbon; Global change; Acid hydrolysis

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1. Introduction

Soil organic carbon (SOC) is a complex mixture of materials that includes plant residues with known constituents, such as cellulose and lignin as well as amorphous, humified-condensation products. The plant residues, soil biota and associated metabolites have mean residence times (MRT) that are measured in months; these constitute the active fraction of SOC. A large slow (intermediate) pool persists for years to decades; the resistant pool resists decomposition for centuries to millennia. All fractions contain C, N, S and P. The active and slow pools control nutrient release, and thus play major roles in ecosystem functioning and sustainable agriculture. Knowledge about the C content of the slow and resistant pool is especially important in the interpretation of soil fertility, pedogenesis and modeling soil responses to global change.

The active and slow fractions can be characterized with added tracers such as ^{14}C , ^{13}C and ^{15}N . The growth of crops with C_4 photosynthetic pathway on soil that had previously supported C_3 crops, or growth of C_3 crops on C_4 soil, provides a most useful signal of the decadal turnover rates characterized by the active and slow fractions (Boutton and Yamasaki, 1996; Puget et al., 1995). The resistant or passive fraction is best characterized using naturally occurring atmospheric ^{14}C . Linear accelerator mass spectrometry for carbon dating allows the measurement of small samples and even specific compounds (Huang et al., 1999).

Carbon dating of soils has involved: (1) studies of stratigraphy and Quaternary research (Caseldine and Mathews, 1985), (2) the role minerals and ions have in stabilizing soil organic matter (Monreal et al., 1997), (3) the effects of agriculture and land-use (Campbell et al., 1967; Hsieh, 1992), (4) soil formation (Martel and Paul, 1974), (5) the effect of depth (Scharpenseel, 1976) and (6) environmental effects (Stout et al., 1981). The great range of organic matter components, together with the thousands of years span in mean residence times, requires that soil organic carbon (SOC) components be fractionated into meaningful pools, and their associated flux rates determined. When tracers are not available, the active and slow pools are best characterized by laboratory incubations, where enzymes of the soil biota effectively fractionate the SOC (Collins et al., 2000; Paul et al., 2001). The isolation of the light fraction and particulate organic matter can also be utilized to gain information on the more labile pools (Cambardella and Elliott, 1994) that often contain the active and slow pools as defined by incubation.

Characterization of the resistant fraction has involved humic and fulvic acid separations (Campbell et al., 1967), particle-associated materials (Anderson and Paul 1984; Townsend and Vitousek 1995) and the measurement of long chain aliphatics from leaf wax (Huang et al., 1999). The refluxing of soil in 6 M hydrochloric acid has most often been used to separate the old, resistant component, which can then be carbon dated (Goh et al., 1984; Scharpenseel,

1976; Scharpenseel et al., 1986; Leavitt et al., 1997). The North American Corn Belt soils, so important in food production and global change scenarios, have received little study by carbon dating, but have been extensively characterized utilizing ^{13}C methodology (Gregorich et al., 1995; Puget et al., 1995; Jastrow et al., 1996). The dynamics of a transect of US Corn Belt soils ranging in mean annual temperature from 6.2°C in Minnesota to 12.4°C in Pennsylvania were previously characterized using ^{13}C analysis (Collins et al., 1999) and laboratory incubation (Collins et al., 2000). In this study, we report on the use of naturally occurring ^{14}C to determine the mean residence time of the total SOC as well as the acid-resistant fraction, to depth, in the soil profiles. The information is necessary to help interpret pedological–paleovegetation studies, in agroecological and soil fertility investigations, and to improve the modeling required to ascertain the role of SOC in C sequestration and global change.

2. Materials and methods

Soil samples were obtained from the 0–20-, 25–50- and 50–100-cm depth increments of field plots cropped to continuous corn (*Zea mays* L.) along a mean annual temperature gradient of 6.2–12.4°C temperature transect from Pennsylvania to Minnesota (Table 1). Soils in the eastern portion formed under mixed deciduous forest, soils in the western portion developed under tall-grass prairie (Coupland, 1992). Previous ^{13}C data (Collins et al 1999) show uniformity in the label to depth that indicates the soil was formed under the vegetation native to the site upon cultivation in the mid to late 1980s. Soil parent materials include glacial tills, loess, lacustrine and colluvium deposits. The Lamberton, MN and Arlington, WI sites are situated on Mollisols that developed from glacial till and loess over glacial till, respectively. Lamberton, MN has been cropped to continuous corn since 1960. Prior to 1960, crop rotations incorporated small grains and forages (Huggins and Fuchs, 1997). The Arlington, WI site, has been in continuous corn since 1958 (Vanotti et al., 1997). The Saginaw, MI site, consisted of a corn–corn–corn–sugar beet (*B. vulgaris* L.) rotation on soils developed from glacial lacustrine deposits (Christenson, 1997). The Kellogg Biological Station site at Hickory Corners, MI developed on parent materials derived from glacial outwash. The Ohio sites occur on calcareous, fine-textured glacial till (Dick et al., 1997) and the Pennsylvania site on colluvium–shale parent material (Peters et al., 1997).

Sampling and sample handling were conducted using exceptionally clean equipment in an environment that had never been exposed to ^{14}C . Six 5.4-cm diameter, 100-cm-long cores were composited for the depths given in Table 2. Bulk density was determined from the mass of soil (oven-dry basis) and the core volume for each sample increment. Air-dried soil samples were sieved through a

Table 1

Site location, annual precipitation, mean annual temperature, crop rotation, soil classification and parent material

Site	AP ^a (mm)	MAT ^b (°C)	Geographic location	Plots established (year)	Crop rotation	Soil classification	Parent material
Lamberton, MN	632	6.2	44°14'N 95°18'W	1960	continuous corn ^c	Typic Haplustolls	glacial till
Arlington, WI	793	7.6	43°18'N 89°21'W	1958	continuous corn	Typic Argiudolls	loess/glacial till
Saginaw, MI	788	8.6	43°23'N 84°07'W	1972	corn/corn/corn/ sugar beets ^d	Aeric Haplaquept	lacustrine/till
Kellogg Biol. Station, MI	728	9.0	42°18'N 85°30'W	1986	continuous corn	Typic Hapludalfs	glacial outwash
Hoytville, OH	835	9.5	41°00'N 84°00'W	1963	continuous corn	Mollic Ochraqualfs	glacial till
South Charleston, OH	910	11.9	39°48'N 83°30'W	1963	continuous corn	Aeric Ochraqualfs	glacial till
Rodale, Kutztown, PA	1180	12.4	40°33'N 75°43'W	1981	corn/corn/soybeans ^e / soybeans ^f .	Typic Fragiudalf	colluvium/gray shale

^aAP—annual precipitation.^bMAT—mean annual temperature.^cCorn—*Z. mays* L.^dSugar beet—*Betula vulgaris* L.^eSoy bean—*Glycine max* L.^fWheat—*Triticum aestivum* L.

Table 2
 Characteristics of the 0–20-, 25–50- and 50–100-cm depth increments

Site	Depth (cm)	Fraction (< 2 mm)			Carbon	
		Sand (g kg ⁻¹)	Silt (g kg ⁻¹)	Clay (g kg ⁻¹)	Inorganic (g kg ⁻¹)	Organic (g kg ⁻¹)
Lamberton, MN	0–20	37 (1)	32 (2)	31 (3)	0.07	17.9 (1.0)
	25–50	39 (2)	26 (1)	34 (2)	0.80	8.7 (0.7)
	50–100	40 (2)	26 (1)	35 (1)	5.73	4.3 (0.2)
Arlington, WI	0–20	6 (2)	65 (3)	29 (2)	0.05	17.6 (0.7)
	25–50	4 (1)	66 (2)	30 (3)	0.01	8.5 (0.4)
	50–100	8 (3)	62 (3)	30 (2)	0.01	3.0 (0.2)
Saginaw, MI	0–20	7 (1)	32 (5)	61 (6)	4.90	16.1 (0.3)
	25–50	7 (1)	32 (1)	61 (2)	11.90	6.0 (0.1)
	50–100	5 (1)	30 (3)	65 (2)	13.70	3.1 (0.1)
Kellogg Biological Station, MI	0–20	39 (3)	43 (3)	18 (1)	0.20	10.7 (0.5)
	25–50	51 (5)	26 (4)	23 (2)	0.15	2.6 (0.4)
	50–100	87 (2)	5 (2)	8 (1)	0.04	1.3 (0.2)
Hoytville, OH	0–20	18 (2)	32 (1)	50 (2)	0.11	17.8 (0.7)
	25–50	16 (2)	31 (2)	53 (2)	0.06	8.6 (0.4)
	50–100	17 (2)	30 (1)	53 (3)	1.79	4.3 (0.1)
South Charleston, OH	0–20	18 (1)	49 (3)	33 (2)	0.94	11.1 (0.9)
	25–50	17 (4)	39 (2)	44 (4)	13.40	5.4 (0.4)
	50–80	27 (3)	39 (2)	34 (6)	34.63	4.2 (0.6)
Rodale, PA	0–20	17 (3)	40 (4)	43 (2)	0.30	10.9 (0.1)
	25–50	21 (4)	37 (2)	42 (4)	0.11	7.0 (0.4)
	50–80	20 (3)	39 (6)	41 (5)	0.08	2.2 (0.1)

2-mm screen, and recognizable plant fragments were removed. Soil carbonates were removed by adding 100 ml of 0.25 M HCl to 20 g soil and shaking for 1 h. The concentration of soil carbonate was determined in separate subsamples from the CO₂ evolved in a closed system after addition of 1 M HCl. For carbon dating, 5 g subsamples were mixed with 1.2 g cm⁻³ NaCl solution to remove plant residue fragments and fine roots not removed by the initial sieving. Floating fragments were skimmed off, and the procedure was repeated until no more plant residues floated to the surface. Samples were then rinsed free of salt, dried, examined under a 20 × microscope to further remove any identifiable plant particulate matter, and then ground with a mortar and pestle.

The residue of acid hydrolysis determined the size of the resistant C (NHC) pool (Leavitt et al., 1997). Acid hydrolysis consisted of refluxing 1–3 g soil with 6 M HCl for 16 h; after filtration, the residue of hydrolysis was washed with deionized water until free of chlorides. The total soil and the residue of hydrolysis were combusted to CO₂ and the ¹⁴C mean residence time (MRT) was determined with tandem accelerator mass spectrometry (TAMS) at the University of Arizona, NSF Accelerator Facility. Graphite TAMS targets were made by reducing the CO₂ to CO on hot zinc, and then reducing CO to graphite on hot iron (Slota et al., 1987). Radiocarbon measurements were corrected for isotopic fractionation that may occur in nature or in laboratory preparation using the sample's δ¹³C value as prescribed in standard ¹⁴C dating protocols (Stuiver and Polach, 1977). Results are expressed as fraction modern carbon (fmC), which is the ratio between the ¹³C-corrected radiocarbon activity of the sample and a standard representing the background radiocarbon activity in AD1950. By this convention, a sample with fmC > 1 would have more ¹⁴C than the background activity in 1950 and would be considered younger, whereas samples with fmC < 1 have less ¹⁴C than the 1950 background and would be considered older. Radiocarbon age (MRT in this study) is calculated by the following equation:

$$\text{MRT (years)} = -\left(1/(\ln 2/\tau_{14})\right)\ln(\text{fmC}),$$

where τ_{14} is the radiocarbon half-life. Any fmC values > 1 could also be influenced by effects of artificial inputs of ¹⁴C into the atmosphere associated with aboveground hydrogen bomb testing that peaked in the mid-1960s.

3. Results

The presence of carbonate-C at the surface in greater amounts than at lower depths in some of the soils (Table 2) was attributed to the presence of agricultural lime. Our laboratory routinely removes carbonates to prevent lime-associated C from biasing SOC determinations. The Lamberton (MN), Saginaw

(MI) and the two Ohio soils were formed on calcareous parent materials, and show an increase in carbonate with depth.

The SOC of the cultivated sites clustered into two groups. The KBS (MI), South Charleston (OH) and Rodale (PA) soils contained approximately 11 g C kg⁻¹ of soil in the surface 20 cm (Table 2). The remaining soils (Lamberton, MN, Arlington, WI, Saginaw, MI and Hoytville, OH) had 60% higher C, ranging from 16.1 to 17.9 g C kg⁻¹ soil.

The two prairie-derived soils (MN, WI) differed in the proportion of SOC resistant to acid hydrolysis with depth (Table 3). The loamy MN soil had similar concentrations of non-hydrolyzable C (NHC) at all depths, with an MRT of 1100 years at the surface and 6000 years in the 50–100-cm depth increment. Non-hydrolyzable C was 400 years older at the surface but 1300 years older at depth. The hydrolyzable C fraction of the MN soil had MRTs one-third lower than those of the total SOC.

The WI soil, with more silt on the profile, showed a decrease in NHC from 50% at the surface to 30% in subsurface horizons. Mean residence times of the total SOC increased from 485 years at the surface to 4412 years in the 50–100-cm depth increment. Non-hydrolyzable C at WI dated 2840 years at the surface and 13580 years at depth. This was 9000 years older than that of the total SOC. The MRT of the NHC was an average of 815 years greater than that of the total SOC in the MN soil, but 5100 years greater than the SOC in the finer textured WI soil. The hydrolyzable C fraction (determined by mass balance) in the 0–20-cm depth increment at WI was modern with a ¹⁴C activity of 1.18 fmC. Subsurface horizons at WI also had more ¹⁴C activity than those from MN, suggesting greater translocation of C to depth in addition to a different distribution of C among soil pools at the WI site.

The forest-derived soils had large differences in the proportion of NHC among sites (Table 4). The fine-textured Saginaw (MI) soil contained 57% to 66% NHC at all depths. The loam-textured cultivated soil at KBS (MI) had a

Table 3
Acid hydrolysis and ¹⁴C characterization of agricultural sites of grassland-derived soils

Site	Depth (cm)	Non-hydrolyzable C (%)	Mean residence time		¹⁴ C activity of hydrolyzable C ^a (fmC ^b)
			Total organic C (years)	Non-Hydrolyzable C (years)	
Lamberton,	0–20	49	1100 ± 53	1510 ± 45	0.91
MN	25–50	45	3100 ± 55	3965 ± 65	0.75
	50–100	48	6107 ± 75	7285 ± 90	0.56
Arlington,	0–20	50	485 ± 50	2840 ± 50	1.18
WI	25–50	35	2620 ± 55	7797 ± 65	0.90
	50–100	30	4412 ± 60	13580 ± 110	0.75

^aCalculated by isotopic mass balance.

^bFraction modern carbon.

Table 4
Acid hydrolysis and ^{14}C characterization of agricultural sites of forest-derived soils

Site	Depth (cm)	Non-hydrolyzable C (%)	Mean residence time		^{14}C Activity of hydrolyzable C ^a (fmC ^b)
			Total organic C (years)	Non-hydrolyzable C (years)	
Saginaw, MI	0–20	63	1383 ± 45	2482 ± 54	1.00
	25–50	57	1510 ± 45	4545 ± 60	0.66
	50–100	66	1510 ± 45	9045 ± 85	0.93
KBS, MI Cultivated	0–20	45	546 ± 50	1435 ±	1.06
KBS, MI	0–20	56	422 ± 51	977 ± 50	1.03
Oak Forest	25–50	23	933 ± 67	895 ± 54	0.88
	50–100	22	1712 ± 50	4406 ± 65	0.96
Hoytville, OH	0–20	46	920 ± 53	1770 ± 45	0.96
	25–50	45	2627 ± 55	5660 ± 87	0.91
	50–100	44	6607 ± 79	9875 ± 75	0.70
South Charleston, OH	0–20	49	Modern	347 ± 57	1.05
	25–50	48	2855 ± 50	5067 ± 69	0.91
	50–100	63	3875 ± 50	7725 ± 70	0.97
Rodale, PA	0–20	38	327 ± 50	2026 ± 98	1.07
	25–50	35	3385 ± 60	8205 ± 75	0.82
	50–100	32	6685 ± 85	10,655 ± 90	0.51

^aCalculated by isotopic mass balance.

^bFraction modern carbon.

lower non-hydrolyzable C pool than the adjacent native site. The native soil contained 56% NHC in the surface 20 cm, but less than half as much NHC in subsoil horizons. The SOC associated with the shales of the PA site had low resistance to hydrolysis. The fine-textured soils at Saginaw (MI) and Hoytville (OH) show 4000–5000 years increases in the MRT of the total SOC with depth. The KBS (MI) and South Charleston (OH) soils had both low SOC contents and low MRTs, with the surface 20 cm of South Charleston site being modern. The Rodale (PA) soils had high MRTs and low soil C levels. On average, the 50–100-cm depth increment of the forest-derived soils had a 3000 years greater MRT than that found for the surface horizon. The NHC was, on average, 900 years older than the total soil C in the surface. It was 2208 years older in the intermediate horizon and 3472 years older in the deepest layer. Acid-hydrolyzable C concentrations reflect the input of bomb-derived ^{14}C that is concentrated in this fraction.

The availability of carbon dates from fields in continuous corn with similar management on a range of parent materials made it possible to determine the effect of soil texture on the MRT of soil organic matter. There is a general negative correlation of MRT with sand content in the lower two horizons (Fig. 1a). The greater number of points than site-treatment depth effects reflects the fact that individual replicates were used in the regressions. Factors other than texture control the MRT of the 0–20-cm depth. Clay content shows positive, if somewhat weak, correlation in subsurface horizons (Fig. 1b). Silt did not have significant correlation with the MRTs of total SOC (Fig. 1c). However, silt content was strongly correlated with the MRT of non-hydrolyzable C of the lowest depth (Fig. 1d), where bomb carbon and other environmental factors do not have much effect on the MRT. This could also be attributed to the effect of C originally associated with the loess that forms the parent material on some of these sites. The 0.2% C associated with loess deposits would represent a small proportion of the SOC in surface horizons, but could be significant at depth.

The complex, four-parameter model fit to the total SOC data and its MRT (Fig. 2) reflects the strong effect of soil depth on the MRT. The 0–20-cm depth increment forms one group of MRTs at high SOC concentrations. Regression of the MRT of the NHC against that of the MRT of the total SOC yields a straight line ($R^2 = 0.66$) with an intercept of 1338 years and a slope of 1.41 (data not shown). This showed that on average, the NHC is 1338 years older than the total SOC. Using a single, two-parameter exponential model (Fig. 3), regression analysis was improved ($R^2 = 0.79$, $p < 0.0001$), further indicating that SOC at depth reflects little accumulation of modern C inputs. Collins et al. (1999), using ^{13}C analysis, found that C originating from corn residues at these sites decreased with depth, averaging $< 10\%$ in the 50–100-cm depth increment.

Previous studies of Corn Belt soils (Gregorich et al., 1995; Balesdent et al., 1988; Jastrow et al., 1996) have used the change in the ^{13}C signal resulting from the switch of C_3 to C_4 plants to determine the dynamics of SOM cycling. Most

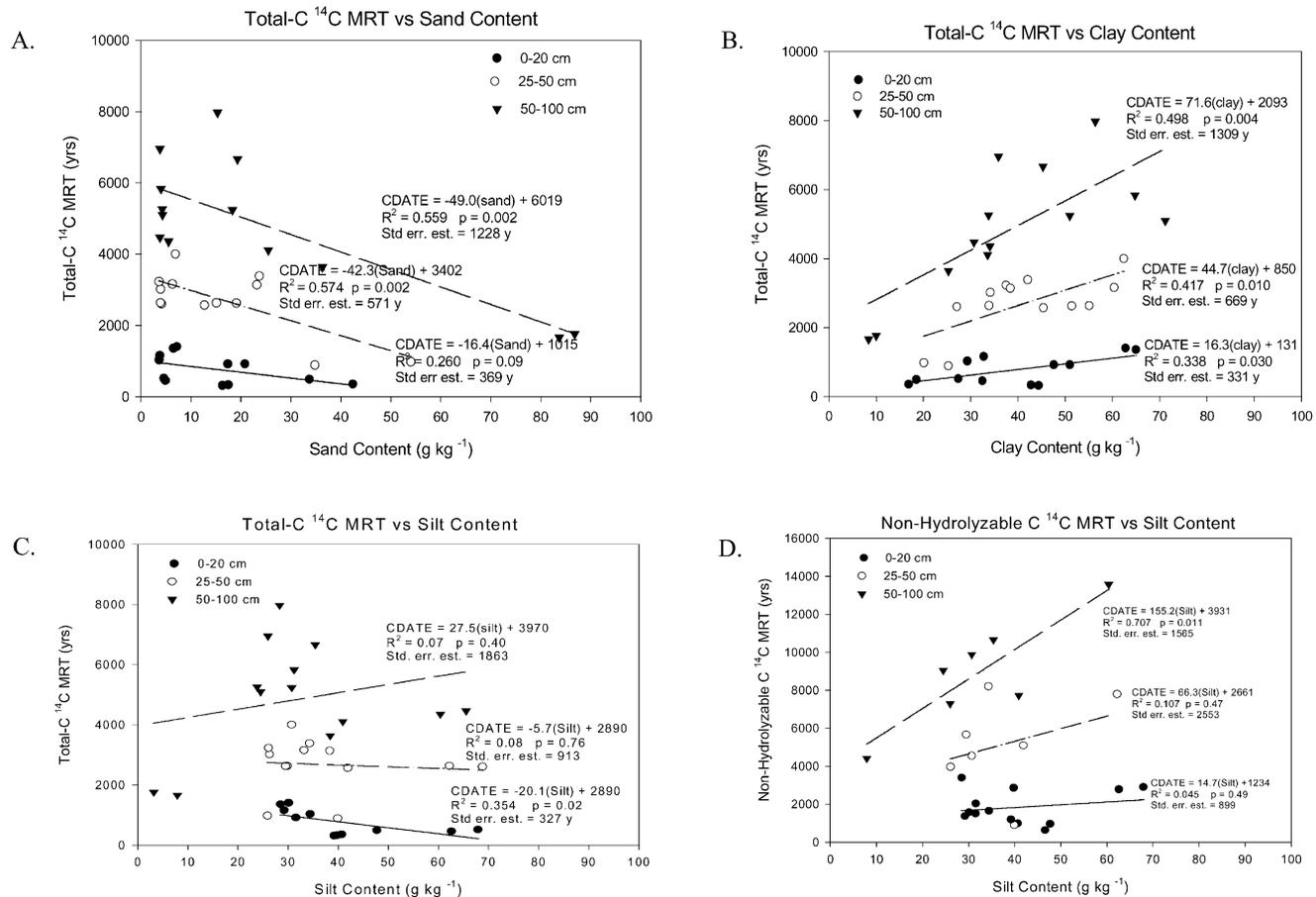


Fig. 1. Relationships between total and non-hydrolyzable ^{14}C with soil particulates.

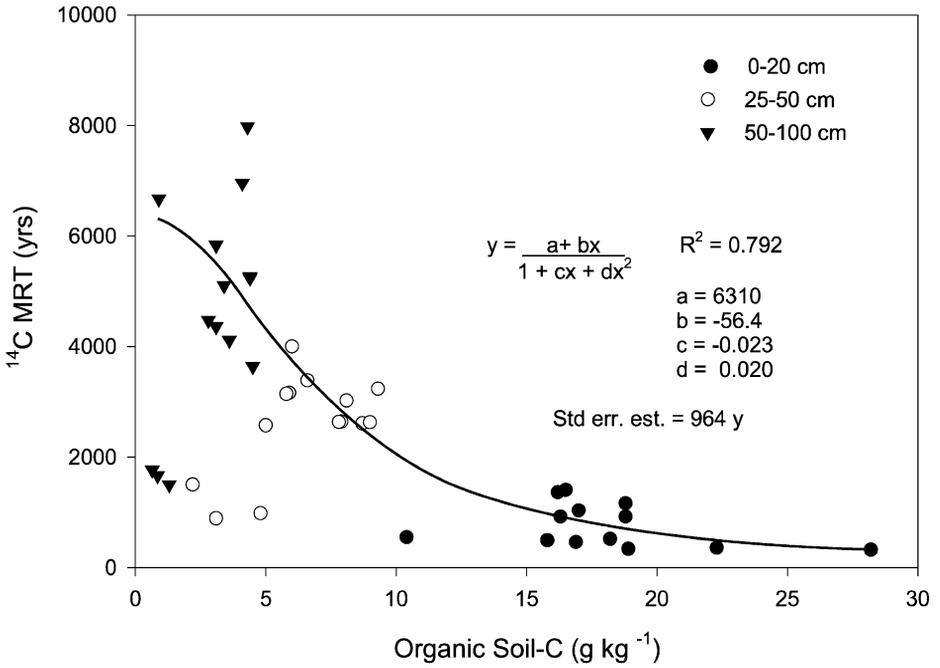


Fig. 2. Relationship between ^{14}C MRT and the content of soil organic carbon.

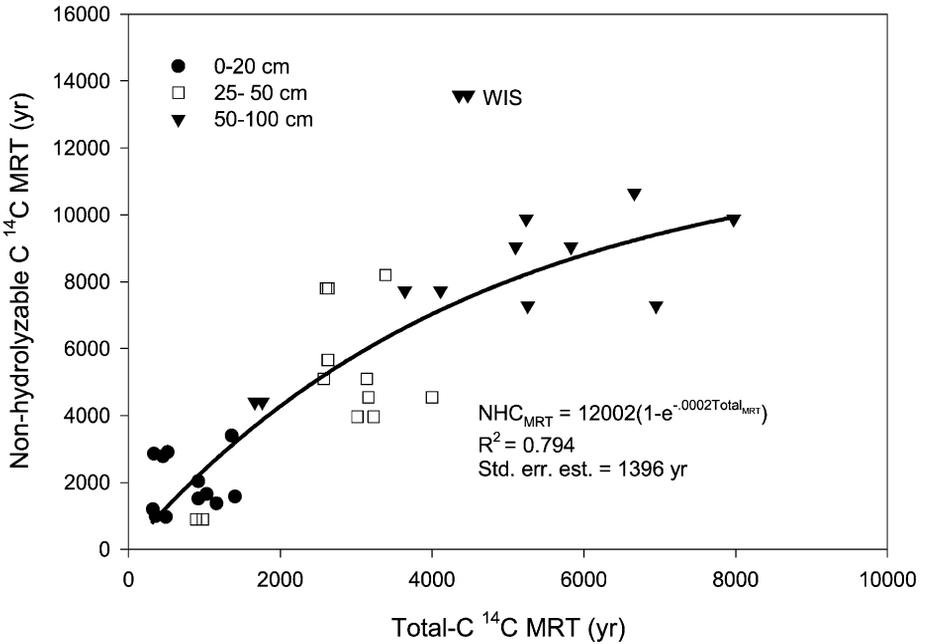


Fig. 3. Relationship between the MRT of non-hydrolyzable ^{14}C MRT with that of the total soil ^{14}C MRT. Regression analysis includes all field replicates except for the WI 50–100-cm depth increment.

of these studies were based on a few years to a decadal time switch in C₃ to C₄ vegetation. It is not known to what extent the lack of uniform incorporation of the ¹³C tracer into all fractions of soil C during the short time frame, relative to the MRT of the total SOC affects the conclusions drawn. The soils utilized in this study had been under continuous corn for 8–35 years depending on the site. We previously analyzed them for their ¹³C contents (Collins et al., 1999). The ¹³C data reflect the dynamics of the active and slow SOC fractions with little labeling of the thousands-of-years-old resistant C fraction. The availability of both ¹⁴C carbon and ¹³C measurements for these soils made it possible to relate our carbon dating data to the previous ¹³C study. The relationship is curvilinear (Fig. 4) with:

$$^{14}\text{C MRT} = 176(^{13}\text{C MRT})^{0.54}$$

The overall curve has an R² of 0.70. The MN site originally formed on a mixture of C₃ and C₄ grasses constitutes an outlier with a low ¹³C age but a high ¹⁴C MRT. Removal of this point improves the regression to R² = 0.76 and lowers the standard error, but does not essentially alter the overall equation. The exponential relationship shows that the wide discrepancy between the two estimates gradually narrows as the MRTs of both increases.

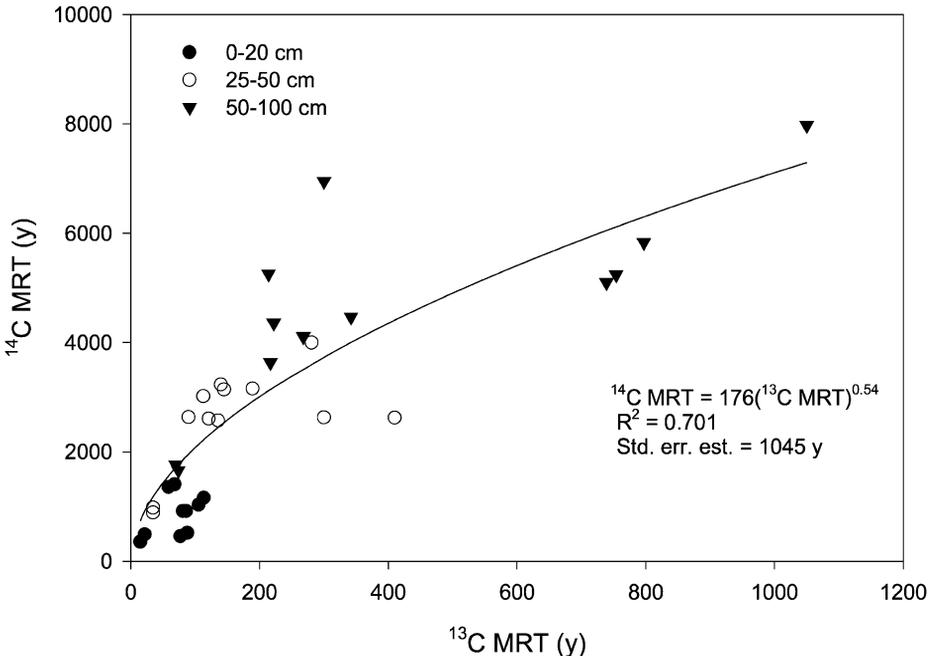


Fig. 4. The relationship between ¹⁴C MRT with that determined with ¹³C after the C₃ and C₄ plants switch to continuous corn (Collins et al., 1999).

4. Discussion

The carbonate content of surface horizons of agricultural soils that had received lime demonstrates that a test for inorganic C should be conducted before the determination of SOC and analysis for either ^{14}C or ^{13}C . The normal acid “fizz test” used to detect pedogenic lime does not detect low levels of agricultural lime, especially if the lime is coarsely ground or contains dolomite. The ^{13}C and ^{14}C signals of agricultural lime are very different than those of soils; errors associated with lime additions would be especially important where tracers are being used to determine SOC dynamics. Low concentrations of lime in semiarid soils are also difficult to detect. We recommend a quantitative analysis for carbonates where there is any possibility of its presence at any soil depth.

We measured the size and turnover of the active (C_a) and slow (C_s) of SOC pool by long-term incubation and measurement of the CO_2 evolved, followed by curve fitting of the data to a three-pool model that includes the resistant NHC (Collins et al., 2000). The NHC was shown in this study to form a significant portion of the SOC. It varies with soil type and depth to such an extent that the size of the resistant pool cannot be ignored during curve fitting of CO_2 evolution data. However, the MRTs of the NHC in this study were all above 350 years. At this MRT, and greater ones, the contribution of the NHC to the CO_2 evolved during laboratory incubation is small (Paul et al., 2001). Carbon dates are expensive and require large, specialized equipment. Calculations (Paul et al., 2001) show that a two-pool, constrained model that utilizes the size of the resistant pool, but not its MRT, if it is above 350 years, gives very similar results to the three-pool model that utilizes the MRT of the resistant fraction. The size of the resistant pool, however, controls the size of the active and slow pool, and thus should be measured.

Our results confirm other studies (Scharpenseel, 1976; Paul et al., 1997) that the MRT of SOC increases significantly with depth. The size of the non-hydrolyzable fraction decreases at lower depths and the C/N ratio often narrows (Stevenson, 1994). This can be explained by the fact that the root-derived substrates that are precursors for humification at depth do not contain the lignin and leaf-wax derived, long chain aliphatics that are present in leaf litter.

There were meaningful relationships between ^{14}C MRTs and primary soil particles that were more significant than the regressions we found between clay and silt contents and the level of total SOC. The often noted, but at times very variable, relation between silt and clay with total SOC content (Burke et al., 1990) could therefore be improved by carbon dating data. Clay content has three possible effects: (1) the direct absorption of organic matter, and thus its protection, (2) the effect of clays on soil cation content and (3) the effect of clay on aggregate formation and stabilization. The strongest association between the content of soil particles and SOC/MRT were noted at depth. This is where

aggregation is usually weakest and indicates that chemical interactions are more important at depth than are physical controls. Aggregation has its strongest effect in the surface horizons where it helps control the MRT of the slow pool that is so essential to soil fertility and decadal C storage (Puget et al., 1995). The NHC with MRTs of centuries and often millennia is important in long-term C storage and in contributing to soil tilth, while having only a small effect on short-term nutrient supplying characteristics.

Silt and coarse clay-sized particulates were earlier shown to be associated with the highest MRTs in soil (Martel and Paul, 1974; Anderson and Paul, 1984). In this study, silt content was correlated with the MRT of the NHC but not of the total SOC. Huang et al. (1999) have related the passive (resistant) fraction of SOC to the content of C₂₅ to C₃₃ alkanes from leaf waxes. These and the acid resistant, persistent aromatics (Skjemstad et al., 1993) do not contain extensive ionic charges. It should not be surprising to find them associated with the coarse clays and silts that are not as reactive as the finer clays.

The great age with depth continues to perplex us. The 30% of the total SOC of the 50–100-cm depth that is non-hydrolyzable in the WI soil developed on loess over till dates over 13000 years. This is equivalent to the time of deglaciation in the last ice age. The high clay substrates of the Saginaw (MI) soil at depth are older than the coarser materials formed on till such as the KBS site. The lower horizons of the fine-textured calcareous soils at South Charleston and Hoytville (OH) also have high MRTs at depth with much older non-hydrolyzable C. The separation of the effect of old SOC transported with the parent materials such as loess from the effects of clays and silt on SOC stabilization requires further study. Soils formed on glacial tills where there would not be any SOC in the parent materials, which generally have lower but still fairly large MRTs, indicating that parent material-derived SOC is not the only explanation for the great MRTs at depth

The importance of SOC in sustainable agriculture and in global change leads to the temptation to predict future scenarios on the basis of individual studies. The relationship of soil C dynamics associated with chemical resistance, as determined by acid hydrolysis, with soil separates, as shown in our clay and silt correlations and with physical–aggregate interactions, is complex. Future global change scenarios are best predicted with simulation models (Parton et al., 1987) that can incorporate the effects of climate, soil characteristics and management using both site-specific and landscape-based information. The results of this study have given us a great deal of most useful pedogenic information. The analytically derived pools and fluxes will be invaluable in future interactive modeling.

The ¹⁴C dating of well characterized sites together with other analysis such as the ¹³C content of soils with a vegetation switch (Collins et al., 1999) and analysis of CO₂ kinetics (Collins et al., 2000) can provide the important information required in answering questions concerning the role of SOC in

global change and sustainable agriculture. Carbon dating also is required because no other labeling studies uniformly label all the SOC constituents. Collins et al. (2000) previously showed a high relationship between the MRT of the slow fraction of SOC as determined with long-term incubation and curve fitting with the field MRT of SOC measured with ^{13}C . In this paper, we further showed the relationship between ^{13}C MRT (Balesdent et al., 1988; Gregorich et al., 1995; Collins et al., 1999) and ^{14}C age. The use of C_3 – C_4 plant switches over periods up to 30 years label only the more labile fractions. In our terminology, this is the active and the slow fraction. However, it does so in a manner that is curvilinearly related to the MRT of the total SOC with the total SOC having an MRT that is 176 times as large as that described by the ^{13}C .

5. Summary and conclusions

The mean residence time of the resistant SOC pool, isolated by 6 M HCl hydrolysis, was determined for several depths at sites across a wide area in the Midwestern Corn Belt. Some of these sites had been native grasslands; others had originally been forested. The percent of soil organic carbon represented by this non-hydrolyzable fraction was generally found to decrease with depth, but in all cases, the MRT increased with depth, in two cases exceeding 10,000 years. The resistant NHC was older than the total (organic) C by an average of 1338 years, but with a pattern of age difference increasing with depth. The MRT of the hydrolyzable C fraction was calculated by mass balance and was usually several hundreds to thousands of years younger than the total SOC. A relationship was developed between the MRT of total-C derived in this study using ^{14}C and in our other study that used ^{13}C . This demonstrated the importance of active and slow pools involved in the relatively short-term ^{13}C studies, and hence, their short overall MRTs that do not adequately represent the MRT of the total SOC. The MRT of total-C was found to decrease in a complex manner with increasing organic C content because of the complex MRT–total SOC–depth interaction.

There was no prevailing difference in percent non-hydrolyzable fraction or MRT of the agricultural soils derived from grassland or forested sites despite the lower overall SOC of the cultivated soils. Some relationships were observed between MRT and soil texture, most notably increasing MRT of total-C with decreasing sand content and increasing clay content. MRT of non-hydrolyzable C increased with silt content in surface soils especially in deeper soil layers.

These results define MRT in the resistant (passive) organic carbon pools with respect to depth, texture, SOC content and MRT of the soil total-C. Although faster-cycling SOC pools may be the targets of C sequestration efforts as well as in sustainable agriculture, a holistic approach including all fractions is needed to fully characterize soil carbon. Efforts to increase sequestration require a better understanding of all SOC pools.

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