



Soil carbon pools and fluxes in long-term corn belt agroecosystems

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Accepted 1 August 1999

Abstract

The dynamics of soil organic carbon (SOC) play an important role in long-term ecosystem productivity and the global C cycle. We used extended laboratory incubation and acid hydrolysis to analytically determine SOC pool sizes and fluxes in US Corn Belt soils derived from both forest and prairie vegetation. Measurement of the natural abundance of ¹³C made it possible to follow the influence of continuous corn on SOC accumulation. The active pools (C_a) comprised 3 to 8% of the SOC with an average field mean residence time (MRT) of 100 d. The slow pools (C_s) comprised 50% of SOC in the surface and up to 65% in subsoils. They had field MRTs from 12–28 y for C₄-C and 40–80 y for C₃-derived C depending on soil type and location. No-till management increased the MRT of the C₃-C by 10–15 y above conventional tillage. The resistant pool (C_r) decreased from an average of 50% at the surface to 30% at depth. The isotopic composition of SOC mineralized during the early stages of incubation reflected accumulations of labile C from the incorporation of corn residues. The CO₂ released later reflected ¹³C characteristic of the C_s pool. The ¹³C of the CO₂ did not equal that of the whole soil until after 1000 d of incubation. The SOC dynamics determined by acid hydrolysis, incubation and ¹³C content were dependent on soil heritage (prairie vs. forest), texture, cultivation and parent material, depositional characteristics. Two independent methods of determining C₃ pool sizes derived from C₃ vegetation gave highly correlated values. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Soil organic matter; Carbon dynamics; ¹³C; Acid hydrolysis; Global carbon change

1. Introduction

Soil organic C (SOC) concentrations reflect soil and ecosystem processes as well as past management of both agricultural and non-agricultural soils. Cultivation has caused reductions in C contents of agricultural soils, contributing to increases in atmos-

pheric CO₂ concentrations. This can be mitigated by incorporation of sustainable management practices such as reduced tillage, decreased bare fallow, increased residue input and conversion to perennial vegetation (Paustian et al., 1997). Determination of the amount of possible mitigation requires an understanding of SOC dynamics. Soil organic matter is composed of a continuum of materials ranging in age from days for plant residues and root exudates to greater than 1000 yr for the resistant, humic substances (Paul and van Veen, 1978; Trumbore et al., 1996). Simulation models describing SOC turnover generally describe the flux of C through pools that decompose according to

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Table 1
Soil series, classification and mean annual temperature by location

Site	Geographic location	Soil series/texture	Classification	MAT (°C) ^a
Lamberton, MN (LMN)	44° 14' N 95° 18' W	Normania loam	Typic Haplustolls	6.2
Arlington, WI (AWI)	43° 18' N 89° 21' W	Plano silt loam	Typic Argiudolls	7.6
KBS, MI (KMI)	42° 18' N 85° 30' W	Kalamazoo loam	Typic Hapludalfs	9.0
Hoytville, OH (HOH)	41° 00' N 84° 00' W	Hoytville silty clay loam	Mollic Ochraqualfs	9.5
Wooster, OH (WOH)	40° 48' N 82° 00' W	Wooster silt loam	Typic Fragiudalfs	9.1

^a MAT = mean annual temperature.

first order kinetics (Parton et al., 1987; Paustian et al., 1992; Buyanovsky et al., 1994). These pools often consist of an active fraction (C_a), a slow fraction (C_s) and a resistant fraction (C_r). Information on SOC dynamics must accurately describe SOC pools and fluxes if models that relate site-specific data to the landscape and interrelate data from multiple sites are to be useful in sustainable agriculture and global C change scenarios.

Carbon dating, after acid hydrolysis, utilizes the naturally-occurring ^{14}C to estimate the mean residence time (MRT) of the old, resistant SOC. This can be combined with ^{13}C analyses and extended incubation of soils from long-term plots to determine pool sizes and fluxes required in C balance calculations. Paul et al. (1997a) found that 70% of the total soil C in 85 y cultivated wheat plots was derived from the native-prairie vegetation. Carbon dating showed the residue of acid hydrolysis to constitute 56% of total C with a MRT of 2600 yr.

The measurement of CO_2 evolution from soil constitutes a bioassay that has been used to determine the effect of environmental variables and management on the decomposition rate of SOC (Collins et al., 1992; Motavalli et al., 1994). This biological fractionation also can be used to measure SOC dynamics. The active fractions (C_a) and a portion of the slow (C_s) pool are degraded by the soil biota and released as CO_2 . Curve fitting of the CO_2 release data can be used to derive estimates for C_a and C_s pool sizes and their turnover rates (Paul et al., in press).

Natural ^{13}C abundance has been used to follow SOC transformations associated with land management (Balesdent et al., 1988; Follett et al., 1997; Collins et al., 1999). The growth of corn or sorghum (C_4) on forest sites (Monreal et al., 1998) or on mixed C_3 – C_4 grasslands (Huggins et al., 1998) are examples of vegetation shifts that provide usable signals (Jastrow et al., 1996). During photosynthesis, C_3 plants incorporate less $^{13}\text{CO}_2$ than do C_4 plants (O'Leary, 1981; Balesdent et al., 1987). Lignin has a different signal than plant carbohydrates (Benner et al., 1987), but there is little discrimination of ^{13}C during microbial attack and humification. The SOC

isotopic composition is comparable to that of the source plant material (Dzurec et al., 1985; Schwartz et al., 1986; Balesdent et al., 1993).

Our objective was to determine SOC pool sizes and turnover rates from a series of long-term agricultural plots with known histories of management and plant residue inputs. The size of the resistant pool (C_r) was estimated from the percentage of C remaining after acid hydrolysis. We used extended, laboratory incubations and curve fitting to determine the kinetics (k_a , k_s) and pool sizes (C_a , C_s) of the active and slow fractions. The $\delta^{13}\text{C}$ measurements of soil and of CO_2 -C evolved during extended laboratory incubations were used to identify the C_3 – C_4 cropping effects and the contribution of incorporated crop residues to SOC pools.

2. Materials and methods

Soils from longterm experimental sites in the Corn Belt region of the East–Central United States (Table 1) were collected in 1992 and 1993 (Paul et al., 1997b; Collins et al., 1999). The most easterly site (Wooster OH) was converted to agriculture in the 1830s, the Michigan site in the middle of the 19th century and the Wisconsin and Minnesota site during the next 20 yr. The poorly-drained Hoytville OH site was not cultivated until after drainage in the early 20th century. All sites had mixed, small grain, corn, forage cropping systems; soybeans were introduced into the rotations in the 1950s.

The Wooster OH silty loam developed under a deciduous forest on fine textured, calcareous, glacial till with a mean annual temperature (MAT) of 9.1°C and 905 mm precipitation. It was sown to a grass meadow in 1957. Continuous corn plots were established in 1963. The poorly drained, silty clay loam, illitic, Mollic soils of the Hoytville site were formed on, deciduous forest intermixed with shrubs and marsh grasses. They were cultivated after installation of drainage tiles; continuous corn was established in 1963. The Kellogg MI site has the coarsest texture with a MAT of 9°C and 932 mm precipitation annually. The

early, mixed grain cropping system with little return of residues resulted in severely degraded soils by 1930. There was some recovery with the incorporation of residues and manure thereafter. Corn was grown in 1986 to 1988, soybeans in 1989 and continuous corn thereafter until the soils were sampled.

The Arlington WI site has a MAT of 7.6°C and 791 mm of rainfall annually. This resulted in an original prairie vegetation on 90 cm deep, loess, deposits over calcareous, loamy, glacial till. The site was in mixed grain with some corn. Any corn residues were burned to facilitate cultivation, for at least 25 yr prior to establishment of the continuous corn, experimental plots in 1958. All residues were then returned to the soil. The most westerly Lamberton MN, originally grassland site, is on fine loamy, glacial drift deposits with a MAT of 6.2°C and 632 mm annual rainfall. Continuous corn, under various N regimes, was established in 1960.

Six cores (5.4 cm × 1 m length) were composited from each field replicate (four replicates at Arlington, WI (AWI); Lamberton, MN (LMN); and Kellogg Biological Station, MI (KMI) and three replicates at Wooster, OH (WOH) and Hoytville, OH (HOH)) using a truckmounted, hydraulic, soil probe. Soil cores were divided into; 0–20, 20–25, 25–50 and 50–100 cm depth increments. The 20–25 cm depth increment is not discussed in this paper. Moist soil samples were sieved to pass a 2 mm screen and recognizable plant fragments removed by hand picking. Soil carbonates were removed by adding 100 ml of 250 mM HCl to 20 g soil and shaking for 1 h. Soils were washed three times with deionized water to remove excess Cl⁻, centrifuged, dried at 55°C and ground to pass a 180 µm screen. Total C and δ¹³C were determined, for duplicate subsamples, on a Europa Model 2020 continuous flow mass spectrometer. Working standards for ¹³C analyses were sugar beet sucrose (-25.68‰ V-PDB) and sugar cane sucrose (-10.45‰ V-PDB) calibrated against NBS-22 (-29.74‰ V-PDB) and ANU sucrose (IAEA-C-6, -10.43‰ V-PDB). Two reference samples were included after every twelfth sample.

Mineralizable soil C was measured during extended laboratory incubation of moist-sieved samples as part of a study, initiated in 1992, that evaluated the effects of agricultural management on SOC contents. Duplicate, 25 g moist-sieved samples of each field replicate were adjusted to 60% water holding capacity and incubated in 160 ml bottles in the dark at 25°C. Water holding capacity was estimated by a volumetric soil water method (Elliott et al., 1994). Briefly, 50 g of sieved (2 mm), air dried soil was packed into 50 cm³ graduated cylinders to a bulk density of 1 Mg m⁻³. Enough water was added to wet the soil halfway up the tube. The soil in the columns was allowed to equilibrate with the water for 24 h, after which the wet soil

was removed and its volume and moisture content determined. Headspace CO₂ was measured using an infra-red gas analyzer (Beckman Instruments, Fullerton, CA) initially at 10 d intervals, later at approximately 21 d intervals. Following CO₂ analysis, each sample was returned to ambient CO₂ by degassing with compressed air.

At the initiation of the ¹³C study, air dry, archived samples were rewetted and incubated to determine ¹³C contents of the evolved CO₂. For archived samples, 75 g of soil were brought to 60% of water holding capacity and incubated in a 0.5 L jar in the dark at 25°C. Samples were conditioned for 10 d prior to the measurement of CO₂ evolution. Evolved CO₂ was trapped in 5 ml, 2 M NaOH. Control jars contained no soil. The trapped CO₂ was precipitated as SrCO₃ using 4 M SrCl₂. The rate of CO₂ evolved was measured by titration of residual NaOH to pH 7.0 with 0.3 M HCl. The SrCO₃ was analyzed for δ¹³C (Harris et al., 1997). The change in δ¹³C-CO₂ released from corn stover without soil was determined by incubating 0.5 g residue mixed with 100 g of sand in a 0.5 L jar, brought to a water potential of 0.33 MPa and incubated in the dark for 50 d at 25°C.

We estimated the size and turnover rates of each pool by curve fitting the CO₂ evolved per unit time using a constrained two pool first-order model:

$$C_{(t)} = C_a e^{-k_a t} + C_s e^{-k_s t}$$

where; $C_{(t)}$ is total C in soil at time t , C_a and k_a represent the active pool, C_s and k_s represent the slow pool. The parameters, C_a , k_a and k_s were estimated using nonlinear regression (PROC NLIN METHOD = MARQUARDT 1995) (SAS, 1995). The slow pool (C_s) was defined as; $C_s = C_{soc} - C_a - C_r$ where C_{soc} was the total SOC at time of sampling. Mean residence time (MRT), the reciprocal (k^{-1}) of the decomposition rate constants, k_a and k_s in first order rate reaction was scaled to field MAT (Table 1) by assuming a Q_{10} that is $(2^{(25-t)MAT/10})$ where MAT is the mean annual temperature. The residue of acid hydrolysis determined the size of the resistant C pool (C_r) (Leavitt et al., 1996). This was determined by refluxing 1 g soil in 6 M HCl for 18 h. Refluxed samples were washed three times with deionized water, dried at 55°C and ground to pass a 180 µm screen. Further details are provided in Paul et al. (in press).

3. Results

3.1. Soil C pools and dynamics

Organic C decreased sharply from surface to subsurface horizons, with 60% of profile C contained in the

Table 2
Total C, resistant C and cumulative C mineralization of cultivated Northern Prairie and Corn Belt soils

Site	Depth (cm)	Total C	Resistant C	Cumulative C mineralization		
		C _T (g kg ⁻¹)	C _r (g kg ⁻¹) ^a	CO ₂ -C (mg kg ⁻¹)	% of total C (%) ^b	
<i>Northern Prairie</i>						
Lamberton, MN	0–20	17.9 (1.0)a	8.8 (0.5)a	1155 (72)a	6.4	
	25–50	8.7 (0.7)b	3.9 (0.4)b	570 (64)b	6.6	
	50–100	4.3 (0.2)c	1.2 (0.1)c	232 (20)c	5.4	
Arlington, WI	0–20	17.6 (0.7)a	8.9 (0.6)a	1279 (78)a	7.3	
	25–50	8.5 (0.4)b	3.0 (0.2)b	400 (22)b	4.6	
	50–100	3.0 (0.2)c	0.9 (0.1)c	120 (10)c	4.0	
<i>Forest</i>						
KBS, MI	CT	0–20	10.7 (0.5)a	4.8 (0.2)a	757 (40)a	7.0
	25–50	2.6 (0.4)b	0.8 (0.1)b	256 (11)b	9.6	
	50–100	1.3 (0.2)c	0.4 (0.1)b	145 (10)c	9.7	
Hoytville, OH	NT	0–20	12.7 (0.8)d	5.8 (0.4)c	815 (32)a	6.4
	CT	0–20	17.8 (0.7)a	8.1 (0.6)a	1027 (54)a	5.8
	25–50	8.6 (0.4)b	3.9 (0.2)b	483 (29)b	5.7	
Wooster, OH	NT	50–100	4.3 (0.1)c	1.9 (0.1)c	242 (10)c	5.5
	NT	0–20	25.6 (1.9)d	10.0 (1.2)d	2051 (120)d	8.0
	CT	0–20	10.9 (0.1)a	4.3 (0.1)a	948 (25)a	8.7
	CT	25–50	7.0 (0.4)b	3.1 (0.2)b	443 (53)b	6.3
	CT	50–100	2.2 (0.1)c	0.7 (0.1)c	123 (10)c	5.6
	NT	0–20	15.5 (0.7)d	6.0 (0.3)d	1460 (103)d	9.4

^a Carbon remaining following a 24 h acid hydrolysis (6 M HCl). CT=conventional till (inversion) NT=no-till. Standard errors of the mean in parentheses. Values within a column by site, followed by the same letter, are not significantly different at $P = 0.05$.

^b Samples incubated for 260 d.

upper 20 cm (Table 2). There were similar distributions of C in prairie- and forest-derived soils. At KMI, 8 yr of no-till increased soil C in the surface 20 cm, 19% above the conventional till treatment. At HOH and WOH, 31 y of no till increased soil C an average of 42%. No-till did not have a significant effect on SOC concentrations below the Ap horizon (data not shown). The proportion of acid-resistant C decreased from 50% of the SOC at the surface to 30% with

depth. No-till increased resistant C by 20% in the surface 20 cm at the KMI, HOH and WOH sites.

The proportion of C mineralized in the surface 20 cm was greater than that mineralized from subsoils, in all but the MI soil (Table 2). Fig. 1 shows the rates of C-mineralized during extended laboratory incubations for the 0–20, 25–50 and 50–100 cm depth increments of the KMI site. Analyses and curve construction were similar for the other four sites (curves not shown). The proportion of SOC in the active pool of CT soils ranged from 2 to 3% in the surface 20 cm of the LMN and AWI prairie sites; the C_a pool accounted and 3 to 6% in the cultivated forest-derived soils (Table 3). The size of the active pool in the surface increased significantly for no till soils at HOH and WOH but not at KMI. The size of the total C pool decreased with depth but the proportion of active C increased below the Ap horizon. At KMI, the C_a pool accounted for 5% of the C in the surface and 8% in the subsurface. Laboratory MRTs of the C_a pool averaged 35 d in the Ap horizon and decreased with depth to 3 to 15 d at 1 m.

The proportion of total C in the slow pool (C_s) ranged from 45 to 50% in the surface 20 cm and increased to an average of 65% in subsoils, except for HOH which showed no change with depth. Field MRTs of the slow pool ranged from 27 to 45 yr in the surface and averaged 24 yr in the subsoil. There was a greater retention of C in the northern prairie soils and

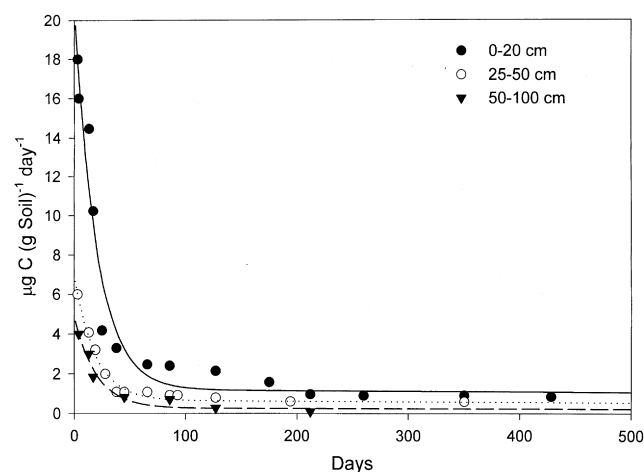


Fig. 1. Rate of CO₂ evolution during extended laboratory incubation of the KMI site.

Table 3

Pool sizes and C-mineralization kinetics of soil for the active and slow C pools from the 0–20 cm, 25–50 cm and 50–100 cm depth increments of the cultivated Northern Prairie and Corn Belt sites

Site	Depth (cm)	Active pool			Slow pool			
		C_a (g kg ⁻¹)	MRT days (d)		C_s (g kg ⁻¹)	MRT (y)		
			lab	field ^a		lab	field ^a	
<i>Northern Prairie</i>								
Lamberton, MN	0–20	0.6 (0.07)a	39 (11)a	148	8.1a	11 (1)a	41	
	25–50	0.3 (0.04)b	17 (2)b	66	4.5b	9 (0.5)b	34	
	50–100	0.2 (0.01)c	3 (0.2)c	11	2.9c	7 (0.2)c	28	
Arlington, WI	0–20	0.4 (0.08)a	27 (7)a	90	8.3a	10 (2)a	33	
	25–50	0.2 (0.06)b	12 (1)b	40	5.3b	13 (1)b	43	
	50–100	0.1 (0.01)c	3 (1)c	11	2.0c	11 (0.4)ab	36	
<i>Forest</i>								
KBS, MI	CT	0–20	0.5 (0.10)a	26 (4)a	78	5.3a	9 (1)a	27
		25–50	0.2 (0.01)b	22 (1)a	67	1.6b	5 (0.1)b	15
		50–100	0.1 (0.01)c	2 (0.1)b	5	0.9c	6 (0.5)b	17
Hoytville, OH	CT	0–20	0.5 (0.05)a	28 (4)a	85	6.3c	11 (1)a	33
		25–50	0.6 (0.07)a	31 (9)a	95	9.1a	15 (2)a	45
		50–100	0.4 (0.06)b	23 (1)b	66	4.3b	13 (2)a	37
Wooster, OH	CT	0–20	0.2 (0.02)c	4 (0.2)c	10	2.2c	7 (0.3)b	21
		25–50	1.8 (0.15)d	75 (7)d	192	12.0d	20 (2)c	58
		50–100	0.6 (0.14)a	52 (5)a	145	6.0a	13 (3)a	39
Wooster, OH	NT	0–20	0.3 (0.03)b	35 (4)b	102	3.6b	13 (1)a	39
		25–50	0.1 (0.01)c	15 (0.3)c	49	1.4c	8 (0.2)b	23
		50–100	1.4 (0.20)d	82 (2)d	247	8.1a	19 (3)a	57

^a MRT = mean residence times converted to field rates using a Q_{10} of 2; $(2^{(25-t)/10})$; where t = mean annual temperature. CT = conventional till (inversion) NT = no-till. Standard errors of the mean in parentheses. Values within a column by site, followed by the same letter are not significantly different at $P = 0.05$.

the increased MRTs in higher clay soils of the forest-derived sites. No-till significantly increased the concentration of C in both the C_a and C_s pools and slowed their turnover at the HOH and WOH sites. Comparisons of the pool sizes and MRTs between moist sieved and air-dried soil samples showed that the size of the C_a pools were similar (Table 4); the MRTs of the active fraction of the moist sieved soils were from 2 to 5 times larger than those of the air dried soils. The MRTs of the slow pool were not significantly different for four of the soils. The MRT of the

slow pool of the WOH site was 13.6 yr for the moist soil but only 8.6 yr for the air dried equivalent.

3.2. ¹³C values of plant materials, soil and evolved CO₂-C

The $\delta^{13}C$ values of forest plant materials were -27.5% for oak leaves (*Quercus rubra*) and -26.5% for oak bark. Corn residues ranged from -12.0% to -12.4% among the sites sampled. Roots were 1‰ less negative than above ground residues. The $\delta^{13}C$ of the

Table 4

Comparison of estimated C-mineralization pool sizes (C_a) and decomposition coefficients (k_a , k_s) of moist-sieved and air-dried soil samples of the 0–20 cm depth increment. Standard error of the mean in parentheses. Significantly different from moist-sieved samples at: * $P = 0.05$, ** $P = 0.01$, *** $P = 0.005$

Site	Moist-sieved			Air-dried		
	C_a (mg kg ⁻¹)	MRT (d)	MRT (y)	C_a (mg kg ⁻¹)	MRT (d)	MRT (y)
Lamberton, MN	639 (42)	54	11.4	648 (26) ^{NS}	18***	10.1
Arlington, WI	382 (38)	39	10.0	300 (15) ^{NS}	8.8***	9.0
KBS, MI	421 (16)	35	8.6	555 (36)*	19.6**	9.0
Hoytville, OH	557 (44)	52	17.4	561 (26) ^{NS}	12***	13.1
Wooster, OH	667 (51)	80	13.6	540 (23) ^{NS}	15***	8.6

Table 5

Change in $\delta^{13}\text{CO}_2\text{-C}$ during extended laboratory incubation of soil from the Lamberton, MN and Arlington, WI cultivated prairie sites. Means significantly different from cultivated samples at *** $P < 0.001$, ** $P < 0.01$ and * $P = 0.05$. nd = not determined

Incubation time (d)	$\delta^{13}\text{CO}_2$ (‰)					
	Lamberton, MN			Arlington, WI		
	0–20 cm	25–50 cm	50–100 cm	0–20 cm	25–50 cm	50–100 cm
10	–12.1a ^a	–13.5b	–15.6c	–11.4a	–13.0b	–16.1c
19	–13.0a	–14.9b	–14.8b	–11.4a	nd	–17.0b
38	–13.0a	–14.9b	–14.6b	–12.3a	–15.7b	–17.3c
66	–13.0	nd	nd	–12.1	nd	nd
93	–13.0a	–15.4b	–16.9c	–12.8a	–16.9b	–16.9b
127	–13.6a	–15.7b	–18.6 ^b	–13.4a	–16.9b	–18.2c
156	–13.7	nd	nd	–13.2	nd	nd
194	–14.7	nd	nd	–13.3	nd	nd
227	–15.5a	–15.7b	–19.1 ^b	–14.4a	–16.9b	–18.1c
353	–15.5	nd	nd	–14.6	nd	nd
<i>Soil samples incubated since 1992</i>						
680				–15.5	nd	nd
739				–15.8	nd	nd
801				–16.5	nd	nd
1110	–15.1	nd	nd			
1169	–16.6	nd	nd			
1292	–17.6	nd	nd			
Cultivated soil	–16.3a	–16.1a	–19.3b	–15.8a	–15.2a	–17.2b
AH soil ^c	–18.4a	–19.1b	–21.4c	–17.7a	–18.2a	–22.8b
Non-cultivated ^d	–19.5***	–19.1***	–19.8*	–17.6***	–17.0***	–18.2*

^a Standard errors of the mean are $< 5\%$. Values within a row by site, followed by the same letter, are not significantly different at $P = 0.05$.

^b Only one sample.

^c $\delta^{13}\text{C}$ of soil following a 24 h acid hydrolysis (6 M HCl).

^d From Collins et al. (1999).

residue of acid hydrolysis was depleted in ^{13}C by 3‰, averaging -15.1% (Collins et al., in press). The $\delta^{13}\text{C}$ values of CO_2 evolved during a 50 d laboratory incubation of corn residues in sand remained nearly constant with an average of -12.2% (data not shown).

Replacement of native vegetation of the prairie (Table 5) and forested sites (Table 6) by mixed cropping and then by C_4 vegetation (corn) resulted in an enrichment in soil ^{13}C in all depth increments especially of the surface samples. The $\delta^{13}\text{C}$ of the surface 20 cm of the soil at LMN changed from -19.5% to -17.6% . At AWI, the corn residue changed the $\delta^{13}\text{C}$ from -17.6 to -15.8% . Cultivated prairie soils, below the Ap, were enriched an average of 1.6‰ above the non-cultivated. The $\delta^{13}\text{C}$ values of the 0–20 cm depth of the cultivated, previously forested sites showed a 3 to 5‰ enrichment compared to the adjacent forested soils (Table 6). Below the Ap the ^{13}C enrichment was 1 to 3‰.

The CO_2 evolved from the 0–20 cm depth increment, during extended laboratory incubations, of the LMN and AWI prairie-derived soils was significantly enriched in ^{13}C early in the incubation, averaging -13% and -12.4% , (Table 5). More than 90% of the CO_2 evolved from d 1 to d 127 was derived from C_4

sources. Following this period, the $\delta^{13}\text{C}$ of the CO_2 from the cultivated soil slowly approached the value of the total soil and surpassed it after 1169 d for LMN and 739 d for AWI. The CO_2 evolved from soil below 20 cm was quickly depleted in ^{13}C approaching the $\delta^{13}\text{C}$ of the whole soil after 93 d. At AWI, below 50 cm, the change to $\delta^{13}\text{C}$ values characteristic of the whole soil occurred within 20 d of incubation.

Values for $\delta^{13}\text{CO}_2$ indicated that initially 50 to 70% of the CO_2 evolved from the previously forested soils was derived from C_4 sources. The $\delta^{13}\text{CO}_2$ evolved from the Ap horizon of KMI was 2 to 4‰ more depleted than either HOH and WHO. This reflects only 8 y of corn growth and the incorporation of one crop of soybeans (-26%) grown during the corn monoculture to eliminate a site weed problem at KMI. The CO_2 evolved from the 0–20 cm depth of the KMI-NT soil was enriched 2‰ above the associated CT soil (Table 7). The $\delta^{13}\text{CO}_2$ of NT and CT soils at HOH and WHO was not different. Both HOH and WHO had been under NT for 31 yr compared to 8 yr for KMI. Calculated field MRTs (Table 3) were shorter for both CT and NT at KMI compared to HOH and WHO, suggesting less stabilization of $\text{C}_4\text{-C}$ into the SOC.

Table 6

Change in $\delta^{13}\text{CO}_2\text{-C}$ during extended laboratory incubation of soil from the KBS, MI, Hoytville, OH and Wooster, OH cultivated Corn Belt sites. Means significantly different from cultivated samples at: *** $P < 0.001$, ** $P < 0.01$ and * $P = 0.05$. nd = not determined

Incubation time (d)	$\delta^{13}\text{CO}_2$ (‰)								
	KBS, MI			Hoytville, OH			Wooster, OH		
	0–20 cm	25–50 cm	50–100 cm	0–20 cm	25–50 cm	50–100 cm	0–20 cm	25–50 cm	50–100 cm
10	-18.6a ^a	-20.3b	nd	-14.2a	-18.6b	-13.7a	-16.7a	-15.7b	-15.9b
19	-18.7a	-20.5b	-18.9a	-14.4a	-19.5b	-14.6a	-16.3a	-16.8a	-16.3 ^b
38	-19.1a	-21.5b	-21.9b	-14.9a	-19.3b	-16.1c	-16.5a	-16.1a	-21.7b
66	-19.1	nd	nd	-16.1	nd	nd	-16.3	nd	nd
93	-19.3a	-21.0b	-22.9c	-16.0a	-18.9b	-16.9c	-16.4a	-18.8b	nd
127	-20.5a	-21.4b	-21.7b	-16.8	nd	nd	-17.3a	-18.5b	-21.1c
156	-21.2	nd	nd	-16.7	nd	nd	nd	nd	nd
194	-21.5	nd	nd	-16.9	nd	nd	-17.6	nd	nd
227	-21.5a	-21.7ab	-22.2b	-17.1a	-21.3b	-22.0 ^b	-18.0a	-18.8b	-21.9c
353	-22.1	nd	nd	nd	nd	nd	-18.2	nd	nd
<i>Soil samples incubated since 1992</i>									
680	-23.4	nd	nd						
739	-22.9	nd	nd						
801	-23.5	nd	nd						
800				-16.7	nd	nd			
800							-21.3	nd	nd
935				-16.9	nd	nd			
935							nd	nd	nd
1058				-19.1	nd	nd			
1058							-22.9	nd	nd
Cultivated soil	-23.1a	-22.0b	-22.7b	-22.1a	-24.1b	-25.6c	-20.3a	-22.1b	-22.3b
AH soil ^c	-25.1a	-24.9a	-25.9b	-24.2a	-25.4b	-27.4c	-23.2a	-24.6b	-24.5b
Non-cultivated ^d	-26.1***	-24.9***	-24.3**	-25.0***	-25.3*	-26.3*	-25.5***	-24.2***	-23.9**

^a Standard errors of the mean are < 5%. Values within a row by site, followed by the same letter, are not significantly different at $P = 0.05$.

^b Only one sample.

^c $\delta^{13}\text{C}$ of soil following a 24 h acid hydrolysis (6 M HCl).

^d From Collins et al. (1999).

Table 7

Change in $\delta^{13}\text{CO}_2\text{-C}$ during extended laboratory incubation in the 0–20 cm depth increment from no-till treatments at KBS, MI, Hoytville, OH and Wooster, OH Corn Belt sites

Incubation time (d)	$\delta^{13}\text{CO}_2$ (‰)		
	KBS, MI	Hoytville, OH	Wooster, OH
10	-16.6 ^a	-14.1	-14.1
19	-16.6	-14.3	-16.7
38	-16.9	-15.0	-16.4
66	-18.3	-15.7	-16.3
93	-18.7	-15.4	-16.8
127	-18.3	-16.9	-17.5
156	-19.3	-16.8	-17.5
194	-20.4	-17.4	-17.8
227	-20.1	-18.6	-18.3
Whole soil	-21.9	-22.6	-20.6
AH soil ^b	-25.1	-24.2	-23.2

^a Standard errors of the mean are < 5%.

^b $\delta^{13}\text{C}$ of soil following a 24 h acid hydrolysis (6 M HCl).

We used the change in $\delta^{13}\text{CO}_2$ to calculate the turnover of C derived from C_3 and C_4 sources (Table 8). The $\text{C}_4\text{-C}$ accounted for 96% of the C_a pool in prairie soils and 82 to 85% of the C_a pool of the forest derived soils after 31 yr corn. The 55% of $\text{C}_4\text{-C}$ in the C_a pool of the KMI site is attributable to a much shorter period in corn. The $\text{C}_4\text{-C}$ accounted for 70% of the C in the slow pool (C_s) at LMN and AWI and averaged 30% for KMI, HOH and WOH. Field MRTs of the $\text{C}_4\text{-C}$, averaged over 1 m depth, were 32 yr for the former prairie and 12 yr for the former forest sites. The MRTs of the $\text{C}_3\text{-C}$ of the C_s pool were two to three times those of the $\text{C}_4\text{-C}$ pool in all soils except HOH where the $\text{C}_3\text{-C}$ pool was seven times that of the $\text{C}_4\text{-C}$. This shows the large resistant C_3 pool in this soil.

There is a relationship of $r^2=0.72$ between the size of the slow (C_s) $\text{C}_3\text{-C}$ pools and estimated MRTs of the C_s pool in the northern, prairie-derived sites (Fig. 2). The correlation for the forest-derived forest soils ($r^2=0.84$) shows that an increase in the MRT increases the pool size. It is impossible to build up the

Table 8

Comparison of pool sizes and C-mineralization kinetics for C₄- and C₃-C pools from cultivated Northern Prairie and Corn Belt sites. np=no pool, nd=not determined or np^a

Site	Depth (cm)	Active Pool				Slow Pool					
		C ₄ -C		C ₃ -C		C ₄ -C		C ₃ -C			
		C _a (mg kg ⁻¹)	Field MRT (d)	C _a (mg kg ⁻¹)	field MRT (d)	C _s (g kg ⁻¹)	field MRT (y)	C _s (g kg ⁻¹)	field MRT (y)		
<i>Northern Prairie</i>											
Lamberton, MN	0–20	640 (20)a	66 (5)a	25 (6)a	8 (1)a	5.5a	28 (2)a	2.6a	59 (3)a		
	25–50	290 (5)b	67 (3)a	36 (5)a	10 (2)a	3.1b	29 (2)a	1.4b	49 (4)b		
	50–100	128 (15)c	15 (2)b	35 (1)a	9 (1)a	1.4c	21 (1)b	1.6b	56 (3)a		
Arlington, WI	0–20	300 (25)a	32 (4)a	np	nd	6.1a	23 (3)a	2.3a	58 (3)a		
	25–50	130 (17)b	42 (2)b	np	nd	4.1b	58 (4)b	1.2b	38 (5)b		
	50–100	41 (2)c	10 (2)c	np	nd	1.3c	32 (2)c	0.7c	31 (2)b		
<i>Corn Belt</i>											
KBS, MI	CT	0–20	310 (17)a	61 (4)a	258 (15)a	58 (4)a	0.9a	15 (2)a	4.3a	38 (2)a	
		25–50	60 (6)b	53 (10)ac	85 (7)b	61 (12)a	0.5b	15 (1)a	1.2b	20 (3)b	
		50–100	54 (2)c	11 (1)b	22 (2)c	18 (1)b	0.2c	4 (1)b	0.7c	16 (3)b	
Hoytville, OH	NT	0–20	311 (15)a	46 (5)c	153 (10)d	82 (5)c	1.7d	26 (8)c	4.6a	51 (5)c	
		CT	0–20	443 (20)a	30 (3)a	94 (6)a	32 (4)a	2.3a	10 (1)a	6.8a	77 (3)a
		25–50	87 (6)b	30 (3)a	212 (13)b	70 (4)b	0.6b	7 (1)b	3.8b	65 (5)b	
Wooster, OH	NT	50–100	80 (1)b	40 (1)b	61 (2)c	16 (2)c	np	nd	2.1c	50 (2)c	
		0–20	1235 (80)c	216 (25)c	435 (30)d	291 (35)d	2.1a	8 (1)a	10.5d	145 (28)d	
		CT	0–20	340 (14)a	67 (15)a	60 (2)a	43 (9)a	1.9a	13 (2)a	3.9a	38 (1)a
	NT	25–50	190 (12)b	102 (12)b	55 (7)a	59 (11)a	0.9b	15 (2)a	2.8b	50 (8)b	
		50–100	68 (12)c	18 (6)c	24 (2)c	5 (1)b	0.3c	13 (1)a	1.1c	24 (1)c	
		0–20	835 (30)d	243 (43)d	300 (25)d	138 (15)c	2.2a	58 (5)c	4.5d	49 (3)b	

^a MRT=mean residence time converted to field rate using a Q₁₀ of 2; (2^{(25-t)/10}); where t=mean annual temperature. CT=conventional till (inversion) NT=no-till. Standard error of the mean in parentheses. Values within a column by site, followed by the same letter are not significantly different at P = 0.05.

C_s pool size without some resistance in the material. The first order model adds a further autocorrelation between the pool sizes and their decomposition rate constants (Paustian and Bonde, 1987). Our analysis shows the prairie-derived soils to have a different form of stabilization than the former forests.

4. Discussion

Our estimates for SOC turnover extend those of other studies that use C mineralization and ¹³C natural abundance to determine the turnover of SOM (Balesdent et al., 1987, 1993; Townsend et al., 1995; Huggins et al., 1998). They also conform to the concept of a three pool, first order SOC model (van Veen and Paul, 1981; Parton et al., 1987) and the knowledge that soils developed under grassland and those on finer textured materials have more resistant SOC components (Gregorich et al., 1995; Buyanovsky et al., 1997; 1994). We show enough interactive effects with climate, parent material, soil depth and the effect of cultivation that prediction models accurate enough for decision making cannot rely on generalizations that are present in most extant models. They require ana-

lytically determined factors, such as those developed here, for at least major subdivisions of the soils involved.

The size of the resistant C pool (C_r), determined by acid hydrolysis, decreased from an average of 50% at the surface to 30% with depth. Of the available fractionation techniques, acid hydrolysis is easy to perform and repeatable. It does not give unambiguous results; some of the lignin from modern plant residues is found in the residue of hydrolysis. This is shown by our data where no-till conducted in the past 30 yr increases the size of the non-hydrolyzable fraction. Although not without problems, acid hydrolysis does differentiate a much older fraction (Leavitt et al., 1996) and was used in this study to determine the size of the C_r pool.

Paul et al. (in press) compared the results of the two pool, constrained model where the size of the resistant pool C_r is used to determine the size of the slow pool C, with those obtained on the same soil with the three pool model. The three pool model can be used when the decomposition rate constant k_r is known from carbon dating of the nonhydrolyzable pool. They found that results from the constrained, two pool model did not differ from that of the three pool model as long

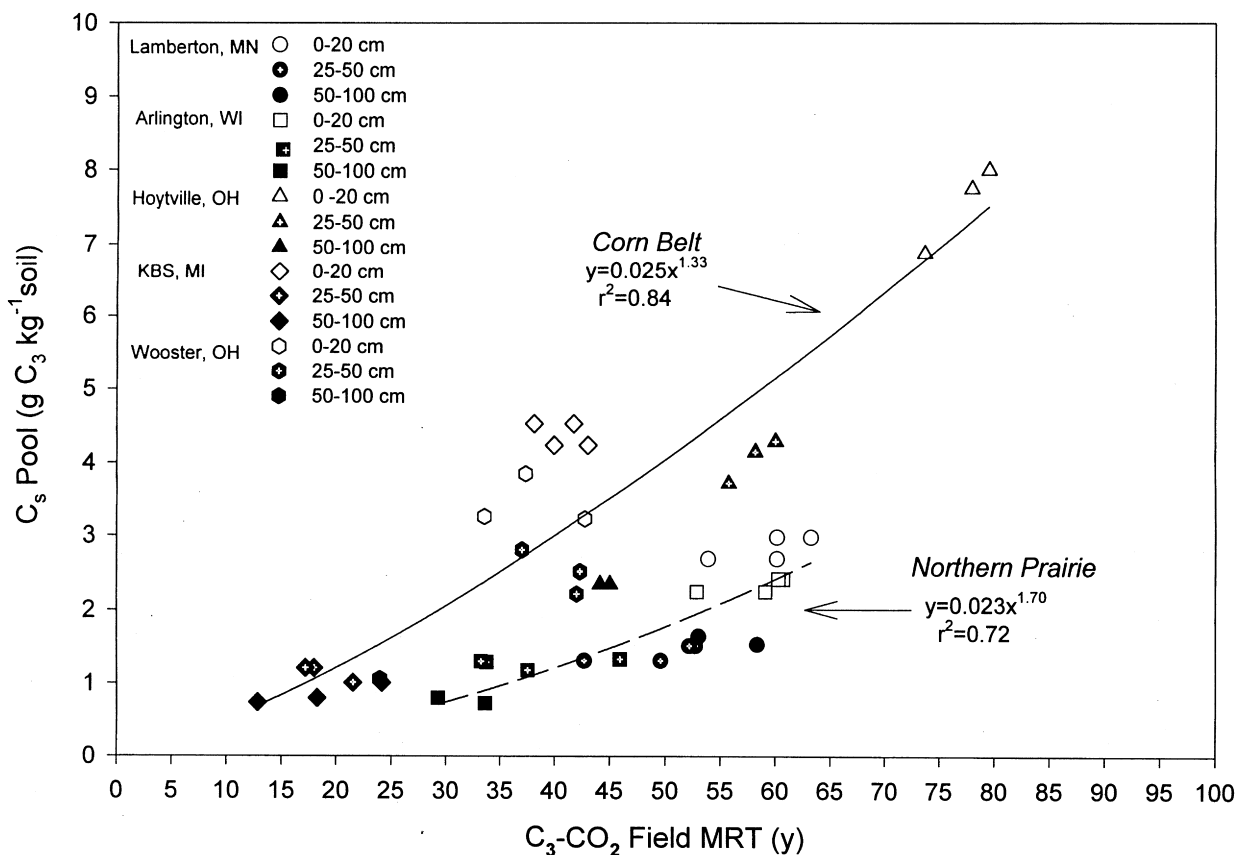


Fig. 2. Relationship between mean residence time (MRT) of the slow pool and its size as determined with incubation and curve fitting.

the MRT of the resistant fraction was 500 yr or older. At this MRT or greater, very little C from this pool is evolved during laboratory incubation and meaningful calculations can be made without the need to carbon date the samples. The size of the C_r pool however must be known. The non-hydrolyzable fraction of the soils described in this paper had average MRTs of 1800 yr (E.A. Paul, pers commun, 1999). The use of a two pool unconstrained model, where the size of C_r was not used to define C_s however did not provide meaningful results (Paul et al., in press).

Extended laboratory incubations of soil with measurements of CO_2 constitutes a biological fractionation of SOC into C_a and C_s pools. The relative contribution of SOC from varying residue sources ($C_3\text{--}C_4$) can be determined by measuring the ^{13}C value of CO_2 produced during incubation. The use of Q_{10} relationships (Townsend et al., 1995; Katterer et al., 1998) makes it possible to convert the laboratory-derived data to field MRTs. The use of a disturbed sample for incubation does not appear to affect results for surface samples. Moisture has not been found to affect the field CO_2 evolution rate of Corn Belt soils (Buyanovsky and Wagner, 1997; Paul et al., 1998).

The MRTs for both the C_a and C_s pools of subsurface samples, incubated in the laboratory, were lower

than expected. Modeling of the field CO_2 measured on a related MI site (Paul et al., 1998), using values established by fractionation techniques similar to those in this paper, produced predicted CO_2 values very similar to field measured values when subsurface MRTs of the C_a and C_s pool were increased by 20% to take into account observations (Coleman et al., 1980) that cellulose strips decomposed 20% less rapidly at depth than in surface horizons. Low MRTs for subsurface samples could also reflect less lignin at depth. This is indicated by less resistance to acid hydrolysis and narrower C-to-N ratios at depth. The lower MRTs, than expected, at depth could also be attributable to less aggregated, deeper soils that decompose rapidly when mixed and brought into the laboratory.

Collins et al. (1999) used field ^{13}C measurements and an exponential decay equation to determine the turnover rate of the $C_3\text{-C}$ within each horizon of the soils utilized in this study. The turnover rates of SOC, ranging from 18 to 100 yr, were related to the length of time the sites have been in corn monoculture as well as to soil texture. That data set allows us to compare the SOC dynamics developed using the techniques utilized in this paper with those on the same soils developed using the field ^{13}C approach (Fig. 3). The pool dynamics measured by curve fitting the $^{13}\text{CO}_2$ evolved

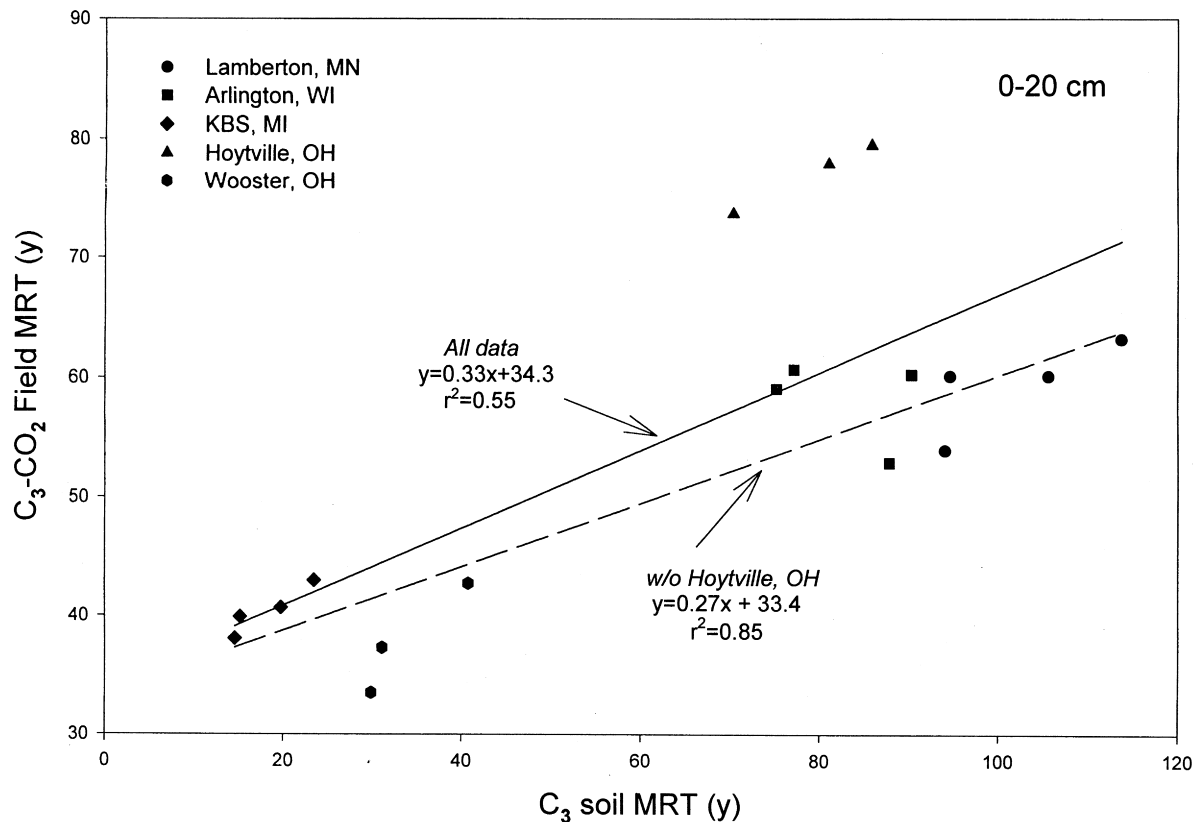


Fig. 3. Relationship between C₃-CO₂ MRT and C₃-C field soil MRT of the 0–20 cm depth increment.

during extended laboratory incubations produced results that were highly correlated to MRTs estimated from the field ¹³C contents. These were calculated by assuming steady state SOC concentrations during corn growth, a drop in C₃-C contents equivalent to the measured C₄ accumulation and first order kinetics.

Patterns of soil C turnover and ¹³C enrichment in these soils resulted from a combination of a change in litter inputs (C₃ to C₄), tillage-influenced redistribution of residue inputs and climate and soil characteristics for each site. Native vegetation at the KMI, HOH and WOH sites, prior to cultivation, was a mixed, deciduous hardwood forest (C₃ photosynthetic pathway) cleared for agriculture in the mid 1850's. The LMN and AWI sites were C₃-C₄ grasslands prior to cultivation. Use of NT increased pool sizes and MRTs in all soils but to different extents depending on soil characteristics.

Carbon mineralized during the early stages of incubation consisted mostly of accumulations of labile C derived from corn residues. This pool contained 3–6% of the total C with an average field MRT of 105 d. The size and turnover of the slow pool (C_s) reflected the degrees of stabilization of C and the effects of management on SOC. The KBS, MI loam soil had the lowest MRTs for both the C_a and C_s pools. The lacus-

trine HOH site had the most stable pools. Longer MRTs for fine textured horizons were observed for the 25–50 cm depth increment at AWI, HOH and WOH. At WOH, this depth increment contained a fine-textured Fragipan that had a C₃-C MRT of 50 yr. The prairie soils showed different dynamics than the previously forested sites.

The analytical determination of pools and fluxes is designed to give estimates of SOC dynamics accurate enough for decision making in sustainable agriculture and global change calculations. Incorporation of information on physical protection through aggregates (Gregorich et al., 1995; Jastrow et al., 1996), in particulate organic matter and the light fraction (Cambardella and Elliott, 1993; Bremer et al., 1994) and interactions with soil primary particles (Amelung et al., 1998) provides additional important information that is especially applicable to the dynamics of the C_s fraction. This must be combined with modeling (to be reported later) that allows calculations of: (1) interpool transfers, (2) the effects of microbial growth efficiencies, (3) climate and (4) residue quality and quantity inputs by both above and beneath ground plant components. Modeling (Paustian, 1992; Motavalli et al., 1994) is also required in transforming site-specific data to a regional basis.

Acknowledgements

The soil samples were obtained from the EPA funded project: *Ecosystem Carbon Pools and Dynamics*) and the Kellogg Biological Station NSF-LTER. The current work was conducted under the auspices of the US Department of Energy grant: *The Measurement of Pool sizes and Flux Rates of Soil Carbon Fractions*. We thank D. Harris for running the ^{13}C analysis.

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