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Chemical composition of soil organic carbon changed by long-term monoculture cropping system in Chinese black soil

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ABSTRACT

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Monoculture is common to meet commodity grain requirements in Northeast China. The effect of long-term monoculture on chemical composition of soil organic carbon (SOC) remains unclear. This study was done to evaluate how changes in chemical compositions of SOC responded to long-term monoculture. To achieve this objective, the chemical compositions of SOC in maize-soybean rotation, continuous soybean and continuous maize were characterized with the nuclear magnetic resonance technique. Two main components, O-alkyl and aromatic C, showed a wider range of relative proportion in monoculture than rotation system across soil profiles, but no difference was observed between two monoculture systems. Pearson's analysis showed a significant relationship between plant-C and OCH_3/NCH, alkyl C or alkyl O-C-O, and the A/O-A was closely related to plant-C. The findings indicated a greater influence of monoculture on the chemical composition of SOC compared to rotation, but lower response to crop species.

Keywords: cultivation; organic carbon composition; soil profile; rotation; continuous cropping

Soil organic carbon (SOC) is a critical factor in adjusting soil fertility and global carbon cycle (Schmidt et al. 2011, Song et al. 2011). To clarify the stability of SOC, some mechanisms have been put forward, including physical, chemical and biological mechanisms (Lützow et al. 2006, Dinakaran et al. 2014). All these mechanisms are linked to inherent molecular structure and composition of SOC (Six et al. 2002, Dhillon et al. 2017). Due to the diverse structure and chemical complexity of SOC (Sutton and Sposito 2005), the information on molecular-level characterization related to SOC stability was limited.

Previous studies showed that major chemical composition of SOC are alkyle C, O-alkyl C, aromatic C, OCH_3/NCH, COO/N-C=O and aromatic C-O (Courtier-Murias et al. 2013, Dhillon et al. 2017). Long- and mid-term traditional tillage increased aromatic C in wheat-sunflower rotation system (Panettieri et al. 2014). Litter decomposition increased the proportions of carboxyl C, alkyl C and aromatic C, and decreased that of O-alkyl C in forest (Zech et al. 1997). Balanced fertilizer increased alkyl-C/O-alkyl-C ratio and decreased aromaticity in maize-wheat rotation system (Xu et al. 2017a), and further improved the aliphatic nature of humin (Chang et al. 2014, Xu et al. 2017b). All these suggested that soil management would change the structural composition of SOC.

SOC derives mainly from plant residues and thus land-cover change will lead to variation in the molecular nature of SOC (Wickings et al. 2012) due to quality and composition of various plant residues. Changes in the amount, structural com-

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position and stability of SOC have been recognized while transferring natural forest or grassland to agricultural land, and vice versa (Guo and Gifford 2002, Solomon et al. 2007, Dhillon et al. 2017). In Northeast China, rotation was changed to monoculture to meet commodity food demand. This study hypothesizes that long-term continuous monoculture might affect chemical structure of SOC, but it may vary with crop species. The aim was to investigate the structural composition of SOC with long-term continuous soybean and maize cropping in black soil farmland in Northeast China, and to explore the potential changes along soil profiles.

MATERIAL AND METHODS

Field experiment. Long-term rotation and continuous monoculture experiments were located at the State Key Agro-ecological Experiment Station, Hailun County, Heilongjiang province, China (47°26'N, 126°38'E). Three cropping systems, including soybean-maize rotation (SM); continuous soybean (CS) and continuous maize (CM), were established for 27 years. The detail field management was the same as local farming practices shown in Miao et al. (2017). Maize roots at 0–20 cm layer were taken out at harvest according to local farming practice.

Sampling. Crops were harvested from three 3.0-m^2 quadrats randomly selected at each cropping plot. Crop biomass was made of aboveground plat parts, litters and roots. The litter under crop was collected using nylon nets placed above the ground during growing season. All crop tissues were washed with water and distilled-water for three times and then oven-dried. Crop tissues were weighed and ground for analyses of SOC and total nitrogen (N) using a CHN analyser (HeraeusElementarVario EL, Germany). All tissues samples were stored in a dryer before analysis.

Soil was sampled randomly using a soil auger at 0–100 cm depth profile under plant sampling, with three points at each plot. Soil of every 20-cm depth was taken as one sample. Samples from the three points constituted one mixed sample and were air-dried; visible vegetation and plant residues were further taken out. Soils were sieved to 2 mm mesh and the subsample was ground for determining total SOC and total N using a CHN analyser (HeraeusElementarVario EL, Germany). At last, soil from field replicates was combined into one composite sample for nuclear magnetic resonance (NMR) measurement.

^{13}C-NMR analysis. Subsequently, composite soil samples along the profile were taken for the ^{13}C-NMR analysis. To remove paramagnetic compounds and concentrate organic carbon, soil sample was mixed and treated with 2% (v/v) hydrofluoric acid (HF). A detailed process was the same as reported by Zhang et al. (2015). Briefly, subsample air-dried composite soil was put into a tube with 40 mL HF. The tube was shaken for 2 h at 25°C, then centrifuged for 10 min at 3000 rpm. Supernatant was poured and the residue was treated with HF for four times. Deionized water was used to remove HF in soil. The final residue was oven-dried at 40°C. The running conditions of (CP/TOSS) and CP/TOSS were the same as reported in Zhang et al. (2015).

Calculation. Plant carbon input was calculated according to the following equation:

$$C_{input} = B_{above-ground} \times C_{above-ground} + \\ + B_{litters} \times C_{litters} + B_{roots} \times C_{roots}$$

Where: B – biomass; C – carbon contents in the aboveground plant parts, litters and roots of soybean or maize.

Aromaticity, the percentage of aromatic carbons, was calculated based on the method of Mao and Schmidt-Rohr (2004).

A/O-A, the alkyl-C/O-alkyl-C ratio, was calculated as (0–44 ppm)/(64–93 ppm).

Statistical analyses. Statistical analyses on replicates of each cropping system were carried out with the IBM SPSS Statistics 22.0 (Armonk, USA). The SOC, total N and plant-C input were analysed by two-way analysis of variance (ANOVA) to elevate the effect of the cropping system and profile depth. All tests were performed at $P < 0.05$.

RESULTS

SOC, TN and plant-C input. After 27-year cropping, the SOC content decreased sharply along soil profile (Figure 1). Lower SOC was observed in long-term monoculture compared to rotation system at 0–60 cm depth. For 0–20 cm depth, the SOC in continuous maize and soybean was lower by 10.1% and 2.7% compared to rotation system, respectively (Figure 1).

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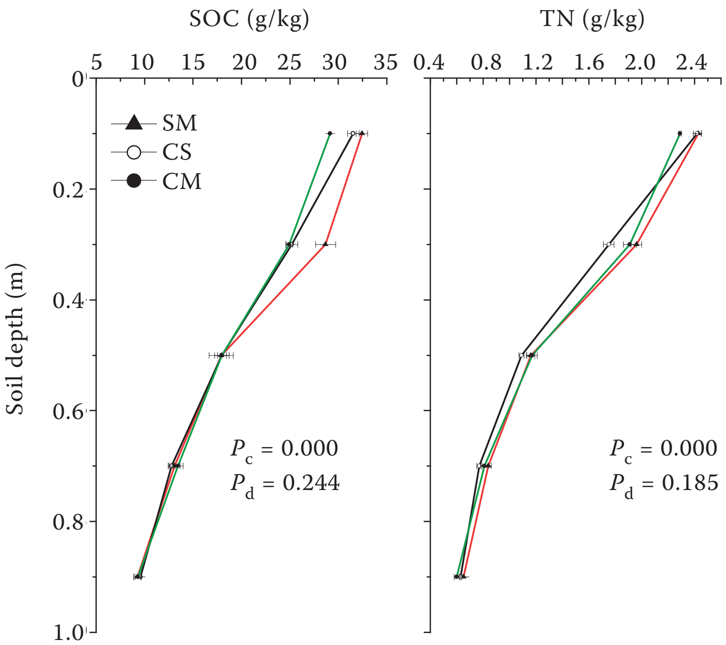

Figure 1. Concentration of soil organic carbon (SOC) and total nitrogen (TN) along the soil profile in soybean-maize rotation (SM), continuous maize (CM) and continuous soybean (CS) cropping system. P_c and P_d – P-value of crops and depth, respectively, with two-way ANOVA at $P < 0.05$

Total N also decreased with soil depths (Figure 1). At the 0–20 cm depth, the concentration of total N in continuous maize system was lower than rotation system, but no difference was found between continuous soybean and rotation system.

Plant-C was mainly distributed at 0–20 cm depth, though continuous maize-C reached to 60 cm depth (Figure 2). The plant-C input at 0–20 cm layer was in the order of CS > SM > CM.

Chemical compositions. The NMR spectra of the soil samples exhibited common signals with different intensity (Figure 3), which resulted in changes of the main C structure. These spectra were separated into eight chemical shift regions and the assignments were as follows: 0–44 ppm, alkyl C; 44–64 ppm, NCH/OCH_3; 64–93 ppm, O-alkyl; 93–110 ppm, alkyl O-C-O; 110–143 ppm, aromatic; 143–163 ppm, O-aromatic; 163–190 ppm, COO/N-C=O; 190–220 ppm, keltones/aldehyde C=O.

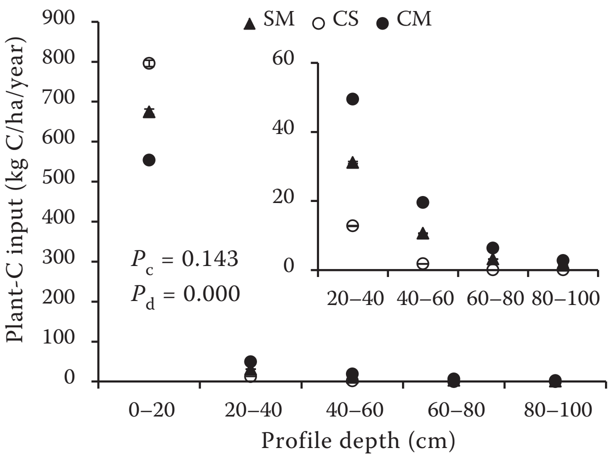

Figure 2. Plant-carbon (C) input along soil profile in soybean-maize rotation (SM), continuous maize (CM) and continuous soybean (CS) cropping system. P_c and P_d – P-value of crops and depth, respectively, with two-way ANOVA at $P < 0.05$

The relative proportions of these functional C groups calculated based on the noise level (Table 1), indicated that O-alkyl C was greatest, followed by aromatic C and nonpolar alkyl C, while the keltones/aldehyde C was the lowest. Compared to rotation, long-term continuous maize cropping increased the proportion of 0–93 ppm shifts, and decreased that of 93–220 ppm shifts at 0–20 cm depth. Long-term continuous soybean increased the proportion of O-alkyl C below 20 cm depth.

Aromaticity and A/O-A. The greatest aromaticity was at 60–80 cm depth and the lowest was at 20–40 cm depth (Figure 4). Compared to rotation, long-term continuous soybean decreased the aromaticity of SOC at 0–40 cm and 80–100 cm depth, but increased that at 40–80 cm depth. Long-term continuous maize decreased aromaticity at 0–60 cm depth and increased it at 80–100 cm depth.

The greatest A/O-A ratio occurred at 0–20 cm depth across the cultivation systems (Figure 4). In contrast, there was a big difference in A/O-A ratio between long-term continuous maize and soybean, except 20–40 cm depth.

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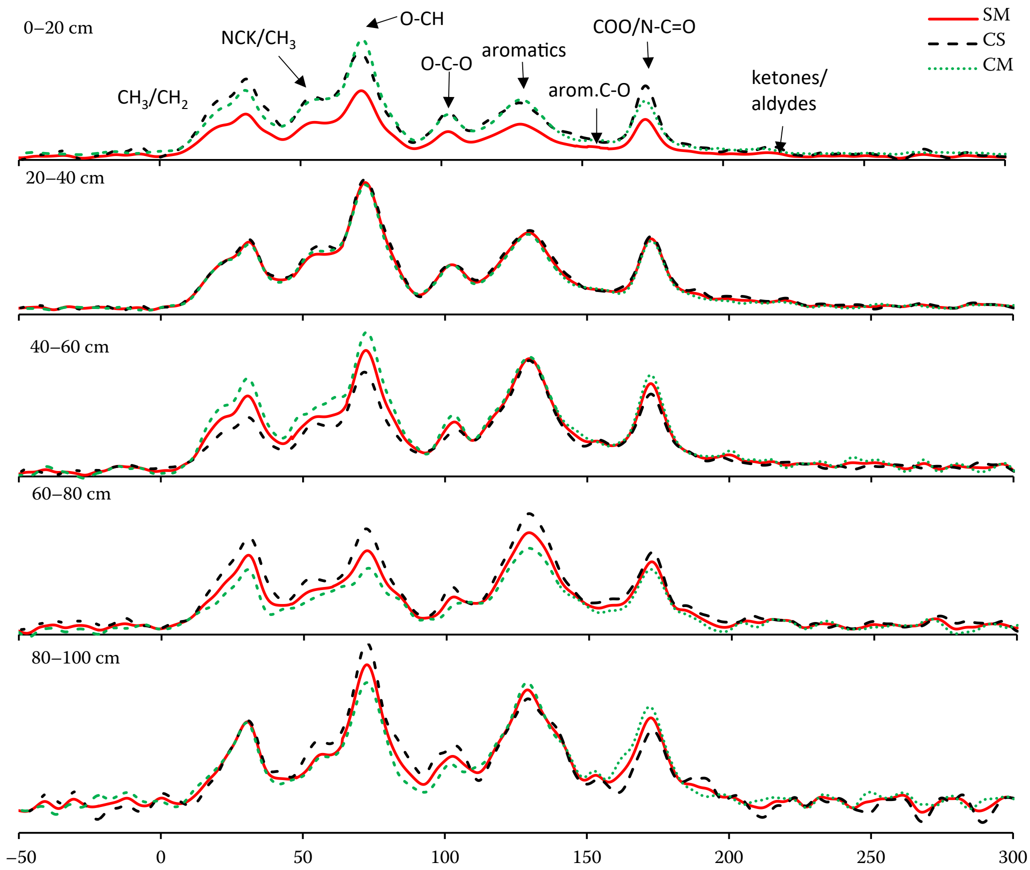

Figure 3. Spectra using unselective CP/TOSS of the soil profile in soybean-maize rotation (SM), continuous maize (CM) and continuous soybean (CS) cropping system

Table 1. Values of relative intensity distributions (%) of carbon composition in soybean-maize rotation (SM), continuous maize (CM) and continuous soybean (CS) cropping system

Treatment	Depth (cm)	0–44	44–64	64–93	93–110	110–143	143–163	163–190	190–220
		nonpolar alkyl C, CH_3,CH&C	methoxy C/N-alkyl NCH/OCH_3	O-alkyl O-CH	alkyl O-C-O	aromatic C-C	O-aromatic C=O	carboxyl/ amide COO/ N-C=O	keltones/ aldehyde C=O
SM	0–20	18.9	11.5	24.0	7.9	17.2	5.2	11.5	3.8
	20–40	15.0	8.5	37.3	5.6	16.4	3.9	10.0	3.4
	40–60	14.3	7.2	34.2	5.2	20.2	4.6	10.7	3.5
	60–80	16.9	6.9	30.6	4.5	22.3	5.0	10.7	3.0
	80–100	13.4	6.5	36.8	5.8	20.2	4.2	11.0	2.2
CS	0–20	23.5	11.4	22.5	7.5	16.1	4.3	11.5	3.2
	20–40	13.6	8.5	41.5	5.0	15.3	3.5	9.3	3.4
	40–60	12.3	7.0	35.0	5.1	21.6	4.8	10.9	3.3
	60–80	18.3	7.8	27.7	4.8	22.6	5.0	10.4	3.4
	80–100	12.4	7.5	40.6	6.7	18.4	3.4	9.3	1.6
CM	0–20	20.3	12.0	25.3	7.6	16.8	4.1	10.3	3.5
	20–40	13.4	8.4	43.6	4.9	14.6	3.6	8.9	2.8
	40–60	15.6	8.6	33.0	5.2	19.0	4.4	10.5	3.7
	60–80	14.6	7.3	33.8	4.2	21.6	4.9	11.0	2.6
	80–100	14.2	6.5	31.9	4.8	22.0	5.1	12.7	2.8

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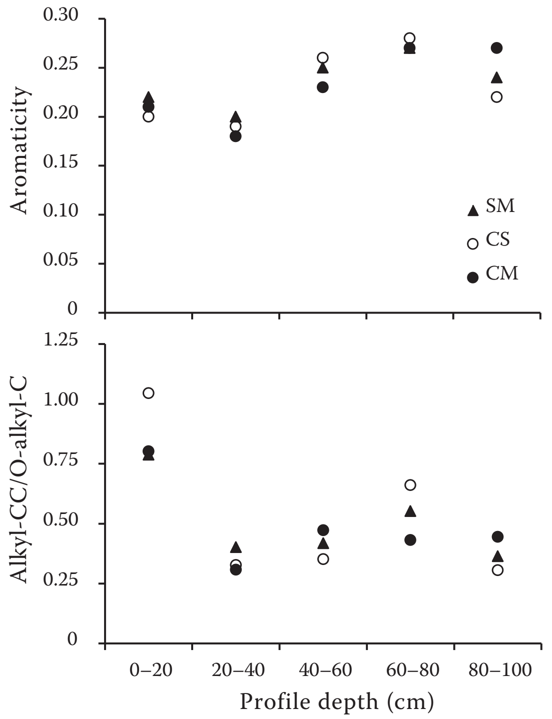

Figure 4. Aromaticity and the alkyl-CC/O-alkyl-C ratio of soil organic carbon along the soil profile in soybean-maize (SM) rotation, continuous maize (CM) and continuous soybean (CS) cropping system

DISCUSSION

Dominance of O-alkyl and aromatic C throughout profile. The largest proportion of O-alkyl C was observed across soil samples (Table 1), which intensified the aliphatic nature of SOC in Chinese black soil. Previous studies reported that O-alkyl C is mainly derived from plant-C and bacterial biomass (Preston and Trofymow 2000, Xu et al. 2017b), and is easily metabolized by soil microorganisms. In the present study, the proportion of O-alkyl C at the surface layer was not positive to plant-C, which indicates that plant-C was not the major resource for O-alkyl C accumulation in the present study. However, long-term cropping increased the light fraction and particle organic matter in our previous studies (Miao et al. 2017), which favours O-alkyl accumulation (Gregorich et al. 2006). In addition, the increase in O-alkyl C might derive from dead microbial populations burst (Cotrufo et al. 2015), due to large amounts of plant residues return after long-term cropping. The O-alkyl C in monoculture system had a wider range of relative proportion than rotation system across soil profiles (Table 1), indicating a great effect of continuous monoculture on O-alkyl C accumulation. The second component is aromatic C, which means that the black soil in Northeast China contains a great amount of black carbon (Nelson and Baldock 2005). Aromatic compounds from plants could not stabilize over a long period in mineral soil (Schöning et al. 2005). Moreover, the decline in aromatic C of monoculture indicated a decreasing trend in a degree of humification (Zech et al. 1997). This was further confirmed especially in 0–20 cm depth by a relatively lower aromaticity and higher A/O-A ratio (Figure 4), which might ascribe to decomposable and unstable SOC from plant residues. From 20 cm to 80 cm depth profile, the decrease in SOC and increase in aromaticity and A/O-A ratio along the profile indicated much more stabilized and intensified humification in deeper soil. However, there was little difference between continuous maize and soybean system. These results support our hypothesis that long-term monoculture may affect the chemical structures of SOC but does not vary with crop species.

Weak relation between plant-C and chemical composition. Three of ten components showed a significant relationship with plant-C, namely alkyl C, OCH_3/NCH and alkyl O-C-O (Table 2). Among them, only NCH/OCH_3 was significantly related to plant-C across the three cropping systems. This is because NCH/OCH_3 is an index of enrichment of fresh ligin, amino acids and proteinaceous materials (Mao et al. 2012). The increased proportion of OCH_3/NCH in monoculture system could be explained by two reasons: first, a decrease in diversity of plant residues would favour the OCH_3/NCH accumulation. Second, carbon sequestration in deeper profiles affects clay content and decreases carbon mineralization (Jobbágy and Jackson 2000). A similar trend in the continuous soybean cropping as maize system was compromised by rich-N soybean residues.

A much closer relationship between plant-C and chemical composition of SOC in monoculture maize than soybean system highlighted that plant residue species has a potential impact on the storage and stability of SOC. Similar results have been found in tropical forest and subtropical grassland ecosystems (Solomon et al. 2007). In this present study, a significant relationship between plant-C and A/O-A ratio further supported our hypothesis (Table 2). In addition, soil organic carbon in the continuous cropping soybean soil is easier to degrade and oxidize than the continuous cropping

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Table 2. Pearson relation analysis for selective index

	Aromaticity	Plant-C	A/O-A	Alkyl C	Methoxy C/N-alkyl NCH/OCH_3	O-alkyl O-CH	Alkyl O-C-O	Aromatic C	O-aromatic C=O	Carboxyl/amide COO/N-C=O	Keltones/ aldehyde C=O
Aromaticity	1										
	1										
	1										
Plant-C	−0.203	1									
	−0.415	1									
	−0.464	1									
A/O-A	0.207	0.909*	1								
	−0.096	0.888*	1								
	−0.259	0.915*	1								
Alkyl C	0.307	0.812	0.967**	1							
	−0.136	0.861	0.992**	1							
	−0.407	**0.943***	0.983**	1							
Methoxy C/N-alkyl NCH/OCH_3	−0.293	0.943*	0.830	0.787	1						
	−0.545	0.954*	0.856	0.868	1						
	−0.721	0.935*	0.813	**0.899***	1						
O-alkyl O-CH	−0.312	−0.864	−0.985**	**−0.933****	−0.743	1					
	−0.234	−0.738	−0.943*	**−0.915***	−0.648	1					
	−0.093	−0.647	−0.896*	−0.820	−0.488	1					
Alkyl O-C-O	−0.549	−0.925*	0.686	0.546	0.884*	−0.621	1				
	−0.658	0.775	0.542	0.501	0.688	−0.351	1				
	−0.583	0.967**	**0.906***	**0.938***	**0.939***	0.649	1				
Aromatic C	0.758	−0.507	−0.216	−0.207	−0.719	0.069	−0.670	1			
	0.930*	−0.477	−0.147	−0.192	−0.633	−0.178	−0.506	1			
	0.869	−0.425	−0.071	−0.216	−0.615	−0.367	−0.460	1			
O-aromatic C=O	0.608	0.621	0.847	0.800	0.437	**−0.922***	0.319	0.307	1		
	0.874	0.069	0.394	0.348	−0.073	−0.669	−0.343	0.762	1		
	0.874	−0.367	−0.016	−0.171	−0.584	−0.415	−0.400	**0.995****	1		
Carboxyl/amide COO/N-C=O	0.026	0.712	0.677	0.491	0.441	−0.745	0.655	0.121	0.728	1	
	0.346	0.694	0.762	0.688	0.516	−0.871	0.302	0.215	0.722	1	
	0.779	−0.224	0.106	−0.068	−0.485	−0.497	−0.209	**0.899***	**0.936***	1	
Keltones/ aldehyde C=O	0.100	0.581	0.602	0.628	0.735	−0.556	0.413	−0.514	0.403	0.036	1
	0.435	0.165	0.336	0.358	0.230	−0.423	−0.493	0.097	0.599	0.481	1
	−0.713	0.487	0.584	0.650	0.658	−0.491	0.658	−0.290	−0.287	−0.184	1

*P = 0.05; **P = 0.01. Three values in one plot represent rotation, monoculture soybean and monoculture maize, respectively

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maize soil. This result might be ascribed to more soybean litters and root residues returned to the surface layer (Miao et al. 2017). All these findings suggested that NCH/OCH_3 and A/O-A ratio could be considered as rapidly respond to changes in cultivation in Northeast China black soil.

REFERENCES

Chang R.R., Mylotte R., Hayes M.H., McLnerney R., Tzou Y.M. (2014): A comparison of the compositional differences between humic fractions isolated by the IHSS and exhaustive extraction procedures. Naturwissenschaften, 101: 197–209.

Cotrufo M.F., Soong J.L., Horton A.J., Campbell E.E., Haddix M.L., Wall D.H., Parton W.J. (2015): Formation of soil organic matter via biochemical and physical pathways of litter mass loss. Nature Geoscience, 8: 776–779.

Courtier-Murias D., Simpson A.J., Marzadori C., Baldoni G., Ciavatta C., Fernández J.M., López-de-Sá E.G., Plaza C. (2013): Unraveling the long-term stabilization mechanisms of organic materials in soils by physical fractionation and NMR spectroscopy. Agriculture, Ecosystems and Environment, 171: 9–18.

Dhillon G.S., Gillespie A., Peak D., Van Rees K.C.J. (2017): Spectroscopic investigation of soil organic matter composition for shelterbelt agroforestry systems. Geoderma, 298: 1–13.

Dinakaran J., Hanief M., Meena A., Rao K.S. (2014): The chronological advancement of soil organic carbon sequestration research: A review. Proceedings of the National Academy of Sciences, India Section B: Biological Sciences, 84: 487–504.

Gregorich E.G., Beare M.H., McKim U.F., Skjemstad J.O. (2006): Chemical and biological characteristics of physically uncomplexed organic matter. Soil Science Society of America Journal, 70: 975–985.

Guo L.B., Gifford R.M. (2002): Soil carbon stocks and land use change: A meta analysis. Global Change Biology, 8: 345–360.

Jobbágy E.G., Jackson R.B. (2000): The vertical distribution of soil organic carbon and its relation to climate and vegetation. Ecological Applications, 10: 423–436.

Lützow M.V., Kögel-Knabner I., Ekschmitt K., Matzner E., Guggenberger G., Marschner B. (2006): Stabilization of organic matter in temperate soils: Mechanisms and their relevance under different soil conditions – A review. European Journal of Soil Science, 57: 426–445.

Mao J.D., Kong X.Q., Schmidt-Rohr K., Pignatello J.J., Perdue E.M. (2012): Advanced solid-state NMR characterization of marine dissolved organic matter isolated using the coupled reverse osmosis/electrodialysis method. Environmental Science and Technology, 46: 5806–5814.

Mao J.D., Schmidt-Rohr K. (2004): Accurate quantification of aromaticity and nonprotonated aromatic carbon fraction in natural organic matter by ^{13}C solid-state nuclear magnetic resonance. Environmental Science and Technology, 38: 2680–2684.

Miao S.J., Qiao Y.F., Li P., Han X.Z., Tang C.X. (2017): Fallow associated with autumn-plough favors structure stability and storage of soil organic carbon compared to continuous maize cropping in Mollisols. Plant and Soil, 416: 27–38.

Nelson P.N., Baldock J.A. (2005): Estimating the molecular composition of a diverse range of natural organic materials from solid-state ^{13}C NMR and elemental analyses. Biogeochemistry, 72: 1–34.

Panettieri M., Knicker H., Murillo J.M., Madejón E., Hatcher P.G. (2014): Soil organic matter degradation in an agricultural chronosequence under different tillage regimes evaluated by organic matter pools, enzymatic activities and CPMAS ^{13}C NMR. Soil Biology and Biochemistry, 78: 170–181.

Preston C.M., Trofymow J.A. (2000): Variability in litter quality and its relationship to litter decay in Canadian forests. Canadian Journal of Botany, 78: 1269–1287.

Schmidt M.W.I., Torn M.S., Abiven S., Dittmar T., Guggenberger G., Janssens I.A., Kleber M., Kögel-Knabner I., Lehmann J., Manning D.A.C., Nannipieri P., Rasse D.P., Weiner S., Trumbore S.E. (2011): Persistence of soil organic matter as an ecosystem property. Nature, 478: 49–56.

Schöning I., Morgenroth G., Kögel-Knabner I. (2005): O/N-alkyl and alkyl C are stabilised in fine particle size fractions of forest soils. Biogeochemistry, 73: 475–497.

Six J., Conant R.T., Paul E.A., Paustian K. (2002): Stabilization mechanisms of soil organic matter: Implications for C-saturation of soils. Plant and Soil, 241: 155–176.

Solomon D., Lehmann J., Kinyangi J., Amelung W., Lobe I., Pell A., Riha S., Ngoze S., Verchot L., Mbugua D., Skjemstad J., Schäfer T. (2007): Long-term impacts of anthropogenic perturbations on dynamics and speciation of organic carbon in tropical forest and subtropical grassland ecosystems. Global Change Biology, 13: 511–530.

Song G.X., Hayes M.H.B., Novotny E.H., Simpson A.J. (2011): Isolation and fractionation of soil humin using alkaline urea and dimethylsulphoxide plus sulphuric acid. Naturwissenschafen, 98: 7–13.

Sutton R., Sposito G. (2005): Molecular structure in soil humic substances: The new view. Environmental Science and Technology, 39: 9009–9015.

Wickings K., Grandy A.S., Reed S.C., Cleveland C.C. (2012): The origin of litter chemical complexity during decomposition. Ecology Letters, 15: 1180–1188.

Xu J.S., Zhao B.Z., Chu W.Y., Mao J.D., Olk D.C., Zhang J.B., Wei W.X. (2017a): Evidence from nuclear magnetic resonance spectroscopy of the processes of soil organic carbon accumulation under long-term fertilizer management. European Journal of Soil Science, 68: 703–715.

Xu J.S., Zhao B.Z., Chu W.Y., Mao J.D., Olk D.C., Xin X.L., Zhang J.B. (2017b): Altered humin compositions under organic and inorganic fertilization on an intensively cultivated sandy loam soil. Science of the Total Environment, 601–602: 356–364.

Zech W., Senesi N., Guggenberger G., Kaiser K., Lehmann J., Miano T.M., Miltner A., Schroth G. (1997): Factors controlling humification and mineralization of soil organic matter in the tropics. Geoderma, 79: 117–161.

Zhang Y.L., Yao S.H., Mao J.D., Olk D.C., Cao X.Y., Zhang B. (2015): Chemical composition of organic matter in a deep soil changed with a positive priming effect due to glucose addition as investigated by ^{13}C NMR spectroscopy. Soil Biology and Biochemistry, 85: 137–144.

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