Supporting Information

for

Abundant and Stable Char Residues in Soils: Implications for Soil Fertility and Carbon Sequestration

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Proof of COO bonding to aromatic rings. We have seen positive evidence that a large fraction of COO groups is bonded to the aromatic rings in the Zook soil HA extract, in terms of cross peaks between aromatic H and COO carbons in two-dimensional ^{1}H-^{13}C (HetCor) spectra (1). Figure S1a shows a two-dimensional ^{1}H-^{13}C heteronuclear correlation spectrum of Hatahara Terra Preta organic carbon. Relevant ^{1}H NMR spectra obtained as partial projections are shown in Figures S1b-e. The spectrum of ^{1}H near the COO groups resonating at 170 ppm, see Figure S1b, shows a dominant aromatic-H peak near 7 ppm (60% of the total area) and a broad shoulder from COOH protons extending to 15 ppm (23%). This confirms that most COO groups substitute aromatic rings, and that many are protonated as a result of HF treatment of the samples.

A shoulder associated with alkyl ^{1}H accounts for 17% of the spectral area in Figure S1b. This component, which according to the spectral pattern in Fig. S1a is mostly associated with COO/NC=O groups resonating around 173 ppm, is enhanced due to the greater proton density of alkyl residues; this is evidenced by a shift of the COO peak from 170 ppm in the DP/MAS spectrum to 172 ppm in the CP/MAS spectrum. According to our decomposition in of Table 1, we expect a fraction of $2/17 = 0.12$ COO or NC=O groups bonded to alkyl groups in soil organic matter not derived from char, in good agreement with the HetCor results taking CP enhancement into account.

Whether the COO groups are bonded to single aromatic rings rather than fused rings can be assessed by H-C dipolar dephasing. Our data show relatively slow dephasing of the COO signals, indicating clustering of aromatic rings and heavy substitution of the rings by COO and O, as in a typical char oxidation product.

^{13}C longitudinal relaxation time in Terra Preta soil organic matter. Figure S2 shows a series of ^{13}C CP NMR spectra of Hatahara Terra Preta soil organic matter after ^{13}C spin-lattice (T_1)

relaxation that proves that longitudinal relaxation is essentially complete within the 40-s recycle delay used in the DP spectra of Figure 1, making those spectra quantitative.

Quantitative analysis of Zook soil humic acid. Table S1 shows the fractions of functional groups in a humic acid extract from the surface horizon of an Iowa Mollisol (Zook, a Cumulic Vertic Endoaquoll) and their decomposition into 67% char residues and 33% other organic matter of moderate aromaticity.

Table S1. Quantitative NMR spectral analysis of Zook Mollisol humic acid extract (based on data from ref. (2)) followed by a possible decomposition into contributions from low-alkyl char residues (of composition similar to those in Terra Preta soils) and from typical soil organic carbon not derived from char (with an aromaticity of 25%). Error margins: ± 2%.

	Carbonyls		Aromatics		Alkyls			
Moieties: ppm:	C=O 210-185	COO / NC=O 185-160	C-OH / C-O-R 160-145	$C_{non\text{-}pro}$ C-H 145 - 100	HCOH / O-C-O 110-50	CH_2 / CH 50-25	CH_3 25-7	**Total**
Zook HA extract	3%	19%	8%	39% 12%	13%	4%	2%	**100%**
Zook HA char residues	2.5%	11%	5%	37% 9%	1%	1%	0.5%	**67%**
Zook HA extract soil org. C	0.5%	8%	3%	2% 3%	12%	3%	1.5%	**33%**

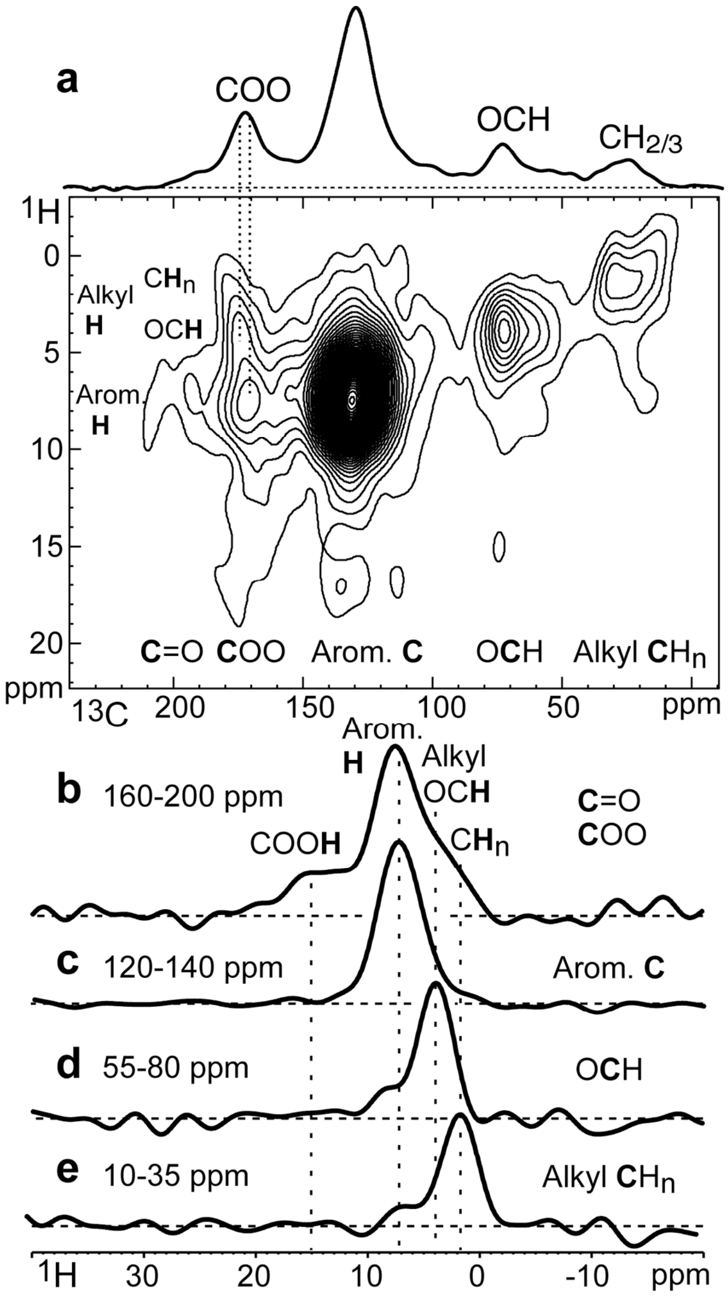

FIGURE S1. (a) Two-dimensional ^1H-^{13}C heteronuclear correlation spectrum of Hatahara Terra Preta soil organic matter with homonuclear (FSLG) decoupling during ^1H evolution and 0.5-ms cross polarization. Spinning frequency: 8 kHz. (b-e) Partial projections showing the ^1H spectrum associated with the carbons observed at (b) 160-200 ppm (COO, C=O, and NC=O), (c) 120-140 ppm (aromatic C), (d) 55-80 ppm (alkyl OCH), and (e) 10-35 ppm (alkyl CH_n). Total measuring time: 42 hours.

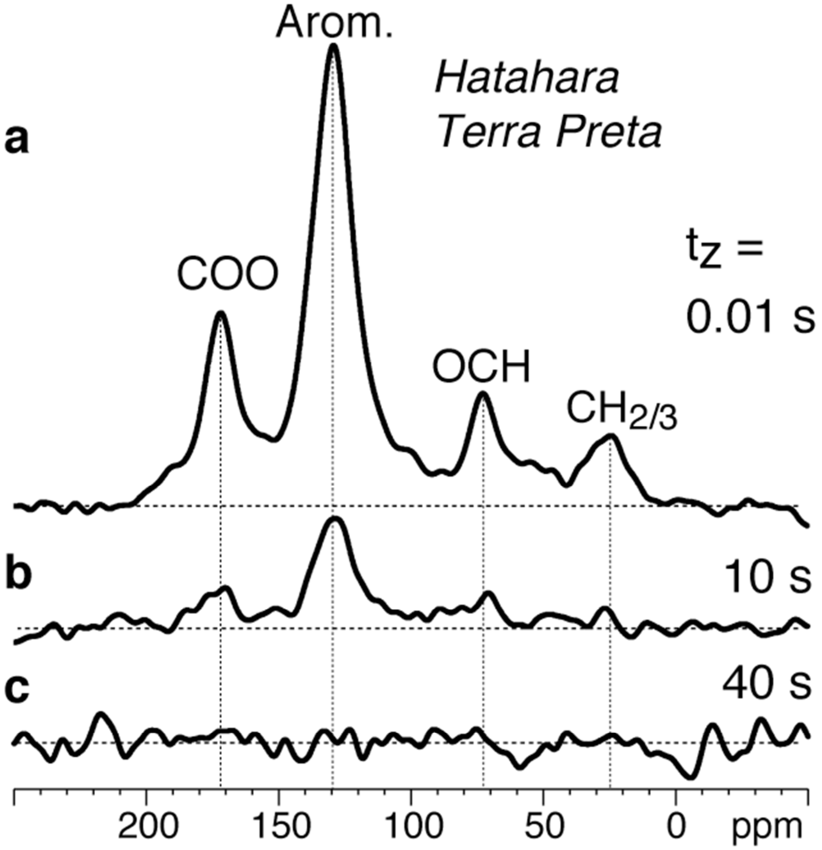

FIGURE S2. Series of ^{13}C CP NMR spectra of Hatahara Terra Preta soil organic matter after ^{13}C spin-lattice (T_1) relaxation during a period t_z of (a) 0.01 s; (b) 10 s; and (c) 40 s, with Torchia's pulse phase cycle (3) that results in zero magnetization for $t_z >> T_1$ ("CP/T_1/TOSS" method (4)). The comparison of the spectra in (a) and (b) shows that most spectral components relax with similar time constants. The absence of detectable signal in (c) proves that the 40-s recycle delay used in the DP spectra of Figure 1 is long enough for essentially complete relaxation of all types of ^{13}C in the sample.

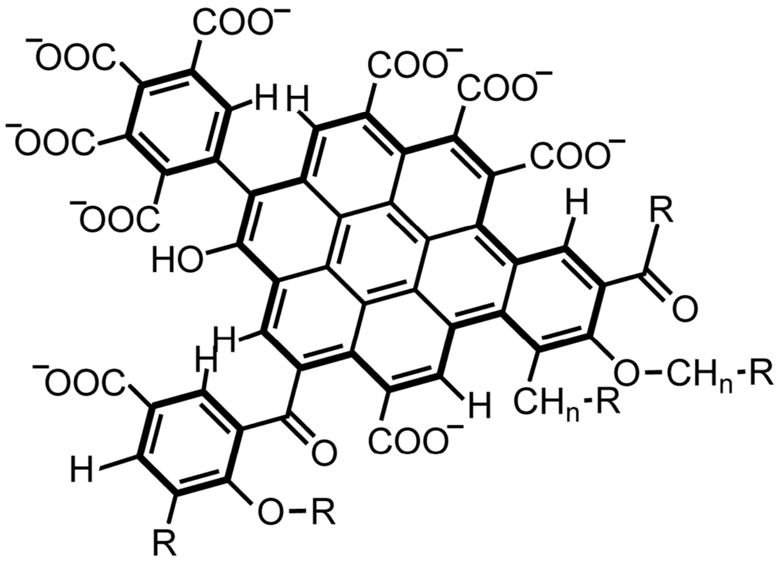

FIGURE S3. Alternative model (to be compared to Figure 3) of a typical stable and fertile aromatic cluster in Terra Preta and temperate grassland soils, consistent with NMR spectroscopy and H-C distance measurements. The cluster of eight fused rings (compared to six in Figure 3) combined with the two single aromatic rings reproduces the measured aromatic edge fraction and is consistent with the observed fairly slow ^{1}H-^{13}C dipolar dephasing.

Literature Cited

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