ORIGINAL ARTICLE

European Journal of
Soil Science **WILEY**

Vertical SOC distribution and aromatic carbon in centuries old charcoal-rich Technosols

Alexander Bonhage[1] | **Thomas Raab**[1] | **Anna Schneider**[1] |
Thomas Fischer[2] | **Shaghayegh Ramezany**[1] | **William Ouimet**[3] |
Alexandra Raab[1] | **Florian Hirsch**[1]

[1]BTU-Cottbus-Senftenberg, Chair of Geopedology & Landscape development, Senftenberg, Germany

[2]BTU-Cottbus-Senftenberg, ZAL, Senftenberg, Germany

[3]Department of Geography, University of Connecticut, Mansfield, Connecticut, USA

Correspondence
Alexander Bonhage, BTU-Cottbus-Senftenberg, Chair of Geopedology & Landscape development, Senftenberg, Germany.
Email: alexander.bonhage@b-tu.de

Abstract

Charcoal-rich Technosols on century-old relict charcoal hearths (RCHs) are the subject of ongoing research regarding potential legacy effects that result from historic charcoal production and subsequent charcoal amendments on forest soil properties and forest ecosystems today. RCHs consist mostly of Auh horizons that are substantially enriched in soil organic carbon (SOC), of which the largest part seems to be of pyrogenic origin (PyC). However, the reported range of SOC and PyC contents in RCH soil also suggests that they are enriched in nonpyrogenic SOC. RCH soils are discussed as potential benchmarks for the long-term influence of biochar amendment and the post-wildfire influences on soil properties. In this study, we utilised a large soil sample dataset ($n = 1245$) from 52 RCH sites in north-western Connecticut, USA, to quantify SOC contents by total element analysis. The contents of condensed highly aromatic carbon as a proxy for black carbon (BC) were predicted by using a modified benzene polycarboxylated acid (BPCA) marker method in combination with diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy-based partial least square regression ($r^2 = 0.89$). A high vertical spatial sampling resolution allowed the identification of soil organic matter (SOM) enrichment and translocation processes. The results show an average 75% and 1862% increase in TOC and BPCA-derived carbon, respectively, for technogenic Auh horizons compared to reference soils. In addition to an increase in aromatic properties, increased carboxylic properties of the RCH SOC suggest self-humification effects of degrading charcoal and thereby the continuing formation of leachable aromatic carbon compounds, which could have effects on pedogenic processes in buried soils. Indeed, we show BPCA-derived carbon concentrations in intermediate technogenic Cu horizons and buried

top/subsoils that suggest vertical translocation of highly aromatic carbon originating in RCH Auh horizons. Topmost Auh horizons showed a gradual decrease in total organic carbon (TOC) contents with increasing depth, suggesting accumulation of recent, non-pyrogenic SOM. Lower aliphatic absorptions in RCH soil spectra suggest different SOM turnover dynamics compared to reference soils. Furthermore, studied RCH soils featured additional TOC enrichment, which cannot be fully explained now.

Highlights

- BC to TOC ratio and high resolution vertical SOC distribution in 52 RCH sites were studied.
- RCH soils non-BC pool was potentially different to reference soils.
- RCH soils feature TOC accumulation in the topmost horizon.
- There is BC translocation into buried soils on RCH sites.

1 | INTRODUCTION

Pyrogenic carbon (PyC) is a broadly defined term that refers to a degradation continuum ranging from lightly charred, relatively easily degradable, to highly condensed aromatic and recalcitrant carbon compounds (Bird et al., 2015)., albeit in this study we refer to the later part of the definition when mentioning PyC. Ongoing discussions point out the difficulty in applying PyC quantification methods to soil samples and interpreting their results, with various studies reporting variability in PyC concentrations of up to orders of magnitude for the same soil samples when applying different methodologies (e.g., Hammes et al., 2007; Kerré et al., 2016; Kurth et al., 2006; Schmidt et al., 2001).

Recent advancements in the discovery and description of pre/early industrial charcoal rich Technosols show their potential to be used as a model system for studying the long-term effects of pyrogenic carbon/biochar additions to soils (Borchard et al., 2014; Burgeon et al., 2020; Criscuoli et al., 2014). The Technosols are found on relicts of historical charcoal production from former upright standing hearths (relict charcoal hearths, RCHs, sometimes also referred to as charcoal kilns), which are mainly found in forests of the humid mid-latitude ecozone in the northern hemisphere. These microrelief sites are circular elevations (on flat terrain) or circular to elliptical levelled platforms (on sloped terrain) with average diameters of approximately 10 metres (Hirsch et al., 2020). Soils on RCHs in the north-eastern USA and Central Europe feature characteristic modifications in soil physical and chemical

properties (Bonhage et al., 2020a; Donovan et al., 2021; Hardy et al., 2016; Hardy et al., 2017a; Hirsch, Raab, et al., 2018a; Hirsch, Schneider, et al., 2018b; Kerré et al., 2017; Mastrolonardo et al., 2018; Raab et al., 2017; Schneider et al., 2018; Schneider et al., 2019), most distinctly, highly increased contents in soil organic carbon (SOC) and a high substrate heterogeneity. Regarding the potential legacy properties of RCHs, increasing attention has been given to floral and faunal composition and abundancies. This discussion started in the mid-1990s by Mikan and Abrams (1995) and Young et al. (1996), who reported primarily negative to neutral effects on tree growth on RCHs. Recent studies report neutral (Mastrolonardo et al., 2019) to negative (Buras et al., 2020; Carrari et al., 2018) effects on tree growth but positive effects on understorey vegetation growth (Carrari et al., 2017). Some studies focus on soil meso- and microfaunal communities in RCH soils and report neutral effects overall and higher abundances of specific nematode communities in affected soils and litter (Gießelmann et al., 2019). Significant changes in soil microbiological and fungal composition have also been described for RCH soils compared to reference soils (Garcia-Berreda et al., 2017; Hardy et al., 2019; Lasota et al., 2021).

The obvious primary driver for the chemical and physical properties of RCH soils is their large content of charcoal and it remains unclear if or to what extent non-PyC dynamics in RCH soils are affected by this. For similar charcoal-rich soils, some studies describe a positive correlation between PyC measured from a variety of methods and total organic carbon (TOC)

TABLE 1 Overview of the commonly applied total organic carbon (TOC) and pyrogenic carbon (PyC) quantification methods used on pre/early industrial relict charcoal hearth (RCH) soils

Study	Methodology	Targeted SOC fractions
Buras et al., 2020, Hirsch, Schneider, et al., 2018b, Carrari et al., 2018, Heitkötter & Marschner, 2015, Criscuoli et al., 2014, Dehkordi et al., 2020, Young et al., 1996	Dry combustion total element analysis	TOC
Hirsch, Raab, et al., 2018a	Dry combustion total element analysis	$PyC_C = RCH\text{-}Ctotal - nonRCH\text{-}Ctotal$
Donovan et al., 2021, Tolksdorf et al., 2020, Bonhage et al., 2020a, Schneider et al., 2020, Schneider et al., 2019, Schneider et al., 2018, Mikan & Abrams, 1995	Loss on ignition (550°C)	TOC
Mastrolonardo et al., 2018	Weak nitric acid digestion (Kurth et al., 2006)	Nonoxidizable SOM
Mastrolonardo et al., 2019, Hardy & Dufey, 2017b	Walkley-Black digestion	Nonoxidizable SOM
Kerré et al., 2016	Acid dichromate oxidation	Nonoxidizable SOM
Kerré et al., 2016	Chemo-thermal oxidation (CTO-285)	Nonoxidizable SOM
Burgeon et al., 2020, Hardy et al., 2019, Hardy et al. 2017a, 2017b, Kerré et al., 2016	Differential scanning calorimetry (DSC)	Charcoal
Hernandez-Soriano et al., 2016	Isotope ratio mass spectrometer	Charcoal derived $\delta^{13}C$ isotopes
Abdelrahman et al., 2018, Borchard et al., 2014	Benzene polycarboxylic acid method (BPCA)	Condensed highly aromatic carbon compounds

concentration (Reisser et al., 2016; Zimmerman & Mitra, 2017). In biochar-rich soils, the effect is mainly attributed to a persistent negative priming effect of PyC on SOC, that is, an enhanced carbon storage caused by the sorption of organic matter on charcoal surfaces that decreases the soil organic matter (SOM) mineralisation rate (Kasozi et al., 2010; Sing & Cowie, 2014; Tilston et al., 2016; Zimmerman et al., 2011). Furthermore, a "self-humification" effect of aged charcoal in soils has been described by some authors (Ascough et al., 2011; Ascough et al., 2020; Cohen-Ofri et al., 2006). Thereby, it can be assumed that the charcoal-influenced carbon pool can be quite dynamic in RCH soils. Indeed, a positive correlation between TOC and PyC concentrations has been described for RCH soils more than 60 years old (Abdelrahman et al., 2018; Borchard et al., 2014) and RCH soils older than 150 years currently under agricultural use (Hernandez-Soriano et al., 2016; Kerré et al., 2017), as have been weathering signs of RCH charcoal (Hardy et al., 2019). Research on RCH soil properties thus far mostly does not differentiate between fractions of the SOC spectrum, with more than half of the studies listed in Table 1 solely reporting total carbon or SOM concentrations. The remaining

studies mainly use wet chemical digestion methods that rely on the oxidisation of nonpyrogenic SOM, resulting in a poorly defined end product, or thermo-gravimetric methods that directly measure CO_2 outputs at charcoal-specific oxidisation temperatures to determine PyC concentrations in soils. The vertical distribution of carbon fractions in RCHs has been poorly studied so far, despite being of potential interest to understand pedogenic processes in charcoal rich soils and to identify leaching and translocation of aromatic carbon, a subject of ongoing research on biochar-amended and wildfire-affected soils (Abney & Berhe, 2018; Bellè et al., 2021; Braun et al., 2020; Hobley et al., 2019).

To better understand the soil carbon dynamics of RCH soils, we utilised the benzene polycarboxylic acid (BPCA) molecular marker method to gain knowledge about the concentration and vertical distribution of aromatic carbon (BPCA-C). BPCA molecular markers are often used as a proxy to determine pyrogenic carbon concentrations in soils. However, current discussions point out that BPCA markers are specific not only for pyrogenic carbon but also for highly aromatic carbon compounds in general (Gerke, 2018; Gerke, 2019).
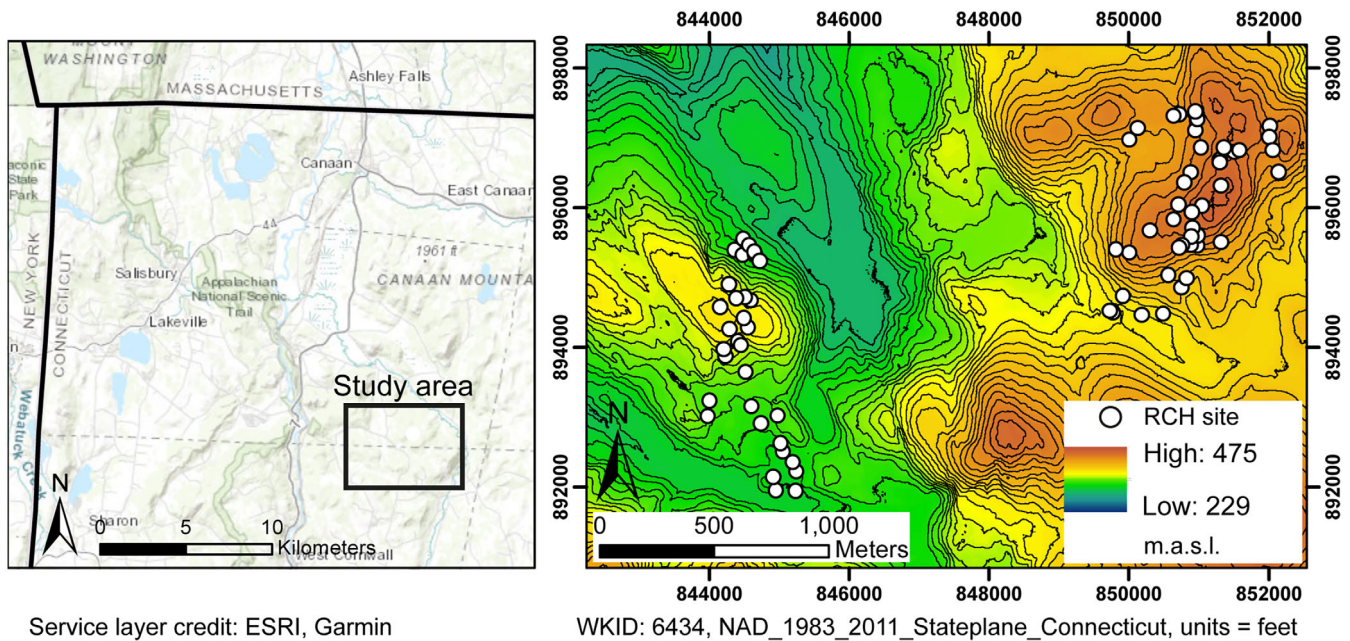
FIGURE 1   Location of the study area in northwestern Connecticut, USA (left) and the locations of 52 sampled RCH sites (right). Digital elevation data curtesy of Connecticut Department of Energy and Environmental Protection (CTECO). 20-metre contour lines are shown

TABLE 2   Natural setting and main properties of the studied soils (data from Raab et al., 2017, Hirsch et al. 2018a, 2018b and this study)

Climate	Temperate
Mean annual temperature	8.3°C
Mean annual precipitation	1350 mm
Vegetation	Mixed forest (Maple, Oak, Birch, Aspen, White Pine)
Reference soils	
Type	Typic dystrudets (US soil taxonomy)/Cambisols (WRB)
Soil acidity (pH) topsoil	3.6–4.7 (4.1)
Average TOC content topsoil	50 g kg^{-1}
Soil texture	Sandy loam
Munsell colour	10 YR 4/2 (dark greyish brown) – 7.5 YR 3.5 (strong brown)
RCH soils	
Type	Anthropic udorthents (US soil taxonomy)/Spolic Technosols (WRB)
Soil acidity (pH) topsoil	3.5–4.8 (4.2)
Average TOC content topsoil	89 g kg^{-1}
Munsell colour topsoil	10YR 2.5/1 (Black)
Period of charcoaling activity	AD 1760–1900

Note: Soil type classification according to US soil taxonomy (Soil Survey staff, 2014) and world Reference Base for soil resources (IUSS working group world Reference Base, WRB, 2014). The soil acidity (pH) in CaCl$_2$ is given as a range and average.

The specific aims of the study are:

- To determine TOC and BPCA-C concentrations in a large RCH- and reference soil sample set ($n = 1245$) using total element analysis and FTIR based chemometric prediction modelling
- To compare TOC and BPCA-C concentrations of RCH-, buried- and reference soil horizons
- To describe the vertical distribution of carbon fractions in RCH soil horizons in high resolution and thereby to study potential redistribution processes and initial pedogenesis in carbon-rich anthropogenic substrates

2 | STUDY SITE AND SOIL PROPERTIES

The study site is located in Litchfield County, northwest Connecticut, United States (Figure 1). The area is part of the Appalachian Highlands, with glacial sediments dominated by till from the Wisconsin glaciation (Stone et al., 2005). The main properties of the study area and its soils are given in Table 2.

A total of 52 RCH sites were sampled on multiple soil profiles (4 soil profiles per site) in vertical 5 cm increments, honouring soil horizon boundaries that have been attributed according to the WRB (Figure 2). Samples were taken volumetrically using 250 ml steel cylinders (8.5 cm × 4.5 cm). Charcoal-rich soil horizons are abbreviated as Auh. Cu horizons consist of
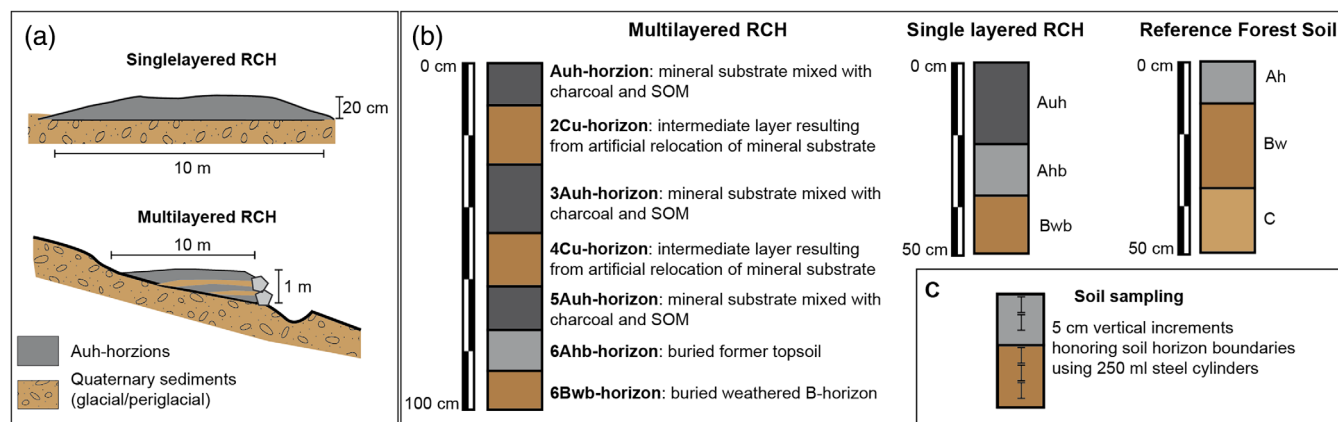
FIGURE 2 (a) RCH site morphology and dimensions; (b) example stratigraphy of RCH sites comprising charcoal-rich technogenic horizons (Auh), relocated mineral substrate (Cu) and buried soils (Ahb, Bwb) as well as reference soils (soil horizon thicknesses not to scale); (c) soil sampling scheme

mineral substrates relocated from adjacent mineral soil horizons (Figure 2, Hirsch et al. 2017). Their origin most likely results from construction to enlarge the platform and level it out. They thereby hint at multiple burning phases of a site (e.g., Raab et al., 2017). Some sites have up to two Cu and three Auh horizons, while other sites are single layered with only one Auh horizon (Bonhage et al. 2020b). Soil horizons buried by the RCH are abbreviated as either Ahb or Bwb, while unaffected reference soil horizons carry Ah and Bw abbreviations.

3 | METHODOLOGY

3.1 | Sample preparation and total carbon analysis

Samples were sieved (<2 mm) and ground to a homogeneous fine powder using a ball mill grinder (Retsch© PM400). Total element carbon and nitrogen analysis was conducted on all samples ($n = 1216$) using an Elementar© vario Max Cube. A subset of samples (BPCA$_{quant}$, $n = 100$) was used for quantifying BPCA-derived carbon. BPCA$_{quant}$ consists of 52 RCH soil samples (Auh and Cu horizons) and 48 reference soil samples (buried A- and B- and non-RCH-affected A- and B-horizons) taken from representative soil profiles. In total, samples from eight sites where included in the BPCA$_{quant}$ dataset, and thereby, no sample from the same depth of every soil profile was included more than once. As we expect a high degree of heterogeneity in the RCH soil, we do not deem pseudo replication to be an issue. To assess the significance of vertical changes of TOC and PyC concentrations we used the nonparametric comparative Mann–Whitney

U tests (SPSS 14, IBM©). We interpreted P values following Muff et al., 2021. Soil acidity (pH) was measured in 0.01 M CaCl$_2$ (1:2.5 w:w).

3.2 | Benzene polycarboxylic acid (BPCA) determination

We applied the benzene polycarboxylic acid (BPCA) molecular marker method originally proposed by Glaser et al. (1998) and modified by Llorente et al. (2018), further modifying the method to allow for the use of microwave pressure digestion. The method aims at cleaving and oxidising benzene rings using nitric acid as well as high temperature and pressure, resulting in aromatic carboxylic acids that can be qualitatively and quantitatively analysed (Chang et al., 2018). For this, 0.5 g of sample material was digested with 10 ml of 4 M trifluoroacetic acid (TFA) (Acros©, CAS: 76-05-1) at 130°C for 30 min in a MARS 6 microwave digestion system (CEM©). The solid residue was then washed three times by repeated centrifugation at 5500 rpm for 10 min, the supernatant was discarded, and fresh distilled water was added each time while stirring. The original protocol used glass fibre filters to separate and wash the solid phase; however, we found the loss of sample material caused by adhesion to the filter to be too high. The washed and dried solid residue was then microwave pressure digested with 6 ml of 65% HNO$_3$ at 200°C for 30 min. The content of the digestion vessels was then filtered using ashless cellulose filters (Whatman© #41, CAT: 1441–110) and washed several times by rinsing with distilled water. The solid phase was discarded. The BPCA-containing solution was then dried at 60°C and rewetted repeatedly to remove nitric acid residues. The solid residue was then weighed,

and its total carbon content was measured by dry combustion. The results are reported as uncorrected BPCA-C concentrations and corrected black carbon (BC) concentrations using a correction factor of 2.27 (Brodowski et al., 2005). The results of the procedure were checked by Fourier-transform infrared (FTIR) spectral analysis of dried residuals from some RCH samples, which confirmed the presence of BPCA-relevant absorption bands. The spectra (Figure S1) show CH bendings and deformations of m, o, p-disubstituted aromatics from 1039 cm^{-1} towards 825 cm^{-1} and lower wavenumbers, aromatic ring C=C stretching at 1481 cm^{-1}, strong C=O stretching at 1668 cm^{-1} and a broad OH stretching at 3500 cm^{-1} that presumably result from residual moisture in the sample material.

3.3 | PLSR-based BPCA prediction

FTIR DRIFT spectra of undiluted soil samples were acquired with a Bruker© Optics (Germany) TENSOR 27 equipped with a DRIFT module, liquid N2-cooled Mercury Cadmium Telluride (MCT) detector and the high-throughput screening extension (HTS-XT) microplate reader. The soil spectra were recorded from 4000 to 400 cm^{-1} and averaged over 40 scans at a 4 cm^{-1} resolution and 10 kHz scan speed. Spectral processing and explorative analysis were conducted using Bruker© OPUS software and the ChemoSpec R package. Spectral bands were assigned using the Wiley's© KnowItAll Informatics System 2020 database or based on literature research. All spectra were baseline corrected and cut at 1300 cm^{-1} to avoid silica band interferences (Robertson et al., 2015). Partial least squares regression (PLSR) and cross validation on the complete dataset were conducted using the OPUS software package. The software's optimisation algorithm was used to find the optimal spectral preprocessing method and the most meaningful wavenumber regions to include in the PLSR analysis.

4 | RESULTS

4.1 | BPCA$_{quant}$ soil properties

Table 3 lists the specific properties of the BPCA$_{quant}$ soil samples. The TOC concentrations of the BPCA$_{quant}$ Auh horizons were approximately twice as high as those of the reference Ah horizons and nearly reached an average of 100 g kg^{-1}. BC made up on average 83% of the TOC concentration in Auh horizons, in contrast to 7% for reference soil Ah horizons. The Auh horizons therefore had an average 75% increase in TOC and an 1862% increase in BC concentrations compared to the adjacent reference topsoil. The Cu horizons had higher TOC and BC concentrations and BC-TOC ratios than all other mineral horizons. The Bw, Bwb and C horizons had comparably low TOC and BC concentrations, resulting in BC-TOC ratios of approximately 30. Ahb horizons, however, had a higher ratio of 54, constituting a 137% increase in BC compared to reference Ah horizons, while their TOC contents were 67% lower.

4.2 | BPCA$_{quant}$ spectral properties

Figure 3 gives an overview of the BPCA$_{quant}$ soil sample spectra. A principle component analysis of untreated BPCA$_{quant}$ spectra showed a separation of scores into two clusters that correspond to the two soil types: RCH soils had mainly positive scores alongside principal component (PC) 1 and negative scores alongside PC 2, while for non-RCH soils, the order was reversed

TABLE 3 Total concentrations of nitrogen (TN), organic carbon (TOC), BPCA-derived carbon (BPCA-C) and black carbon (BC) grouped by soil horizon (mean ± standard deviation) for BPCA$_{quant}$ samples

	Soil horizon	pH in CaCl$_2$	n	[g kg^{-1}]				Ratio
				TN	TOC	BPCA-C	BC	
RCH soils	Auh	3.5–4.8 (4.2)	42	2.4 ± 0.9	94.6 ± 48.1	34.6 ± 21.8	78.5 ± 49.4	83
	Cu	4.4–5.0 (4.7)	8	0.9 ± 0.3	38.4 ± 24.7	11.3 ± 8.0	25.6 ± 18.1	66
Non-RCH soils	Ahb	4.6–4.8 (4.7)	5	0.5 ± 0.1	17.4 ± 4.8	4.2 ± 2.4	9.5 ± 5.4	54
	Ah	3.6–4.7 (4.1)	11	2.1 ± 0.8	53.8 ± 29.0	1.8 ± 1.3	4.0 ± 2.9	7
	Bwb	4.3–5.1 (4.8)	10	0.6 ± 0.2	16.8 ± 5.4	2.7 ± 1.1	5.1 ± 2.4	30
	Bw	4.2–4.9 (4.5)	23	0.7 ± 0.5	13.3 ± 9.4	2.0 ± 1.9	4.5 ± 4.3	33
	C	4.9	7	0.5 ± 0.2	8.6 ± 3.7	1.1 ± 0.5	2.4 ± 1.1	27

Note: Soil acidity (pH) is given as a range and average. The ratio gives the BC to TOC ratio.
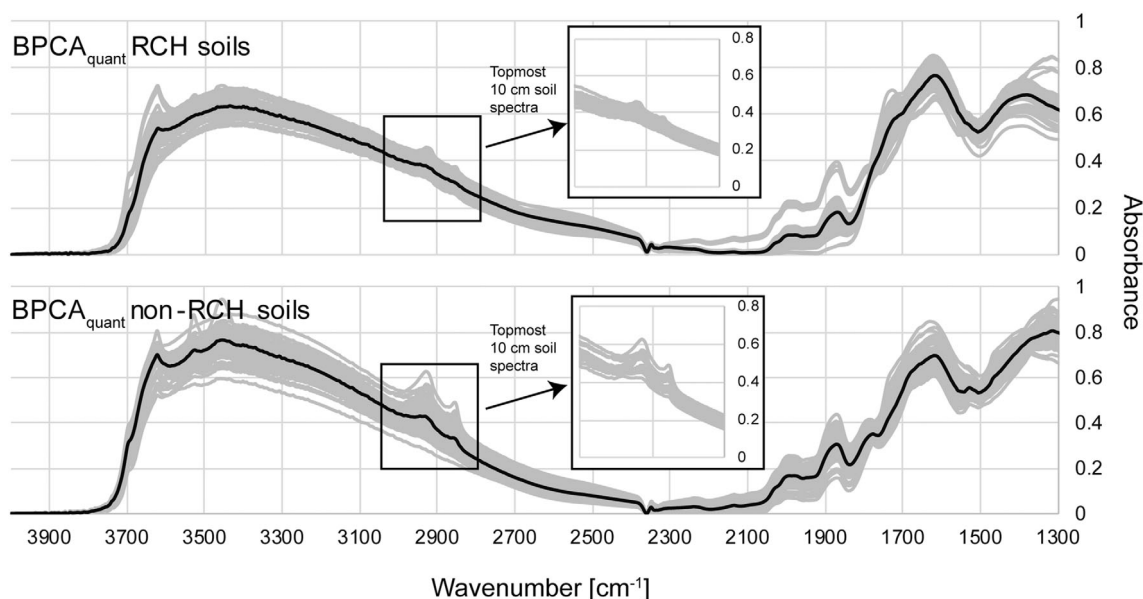
FIGURE 3 Diffuse reflectance spectra of BPCA$_{quant}$ RCH soils (Auh, Cu horizons) and non-RCH soils (Ahb, Bwb, Ah, Bw horizons). The black line shows the averaged spectra. Close ups of the aliphatic CH absorption wavenumber region exclusively show spectra of soil samples taken from the top 10 cm of a soil profile
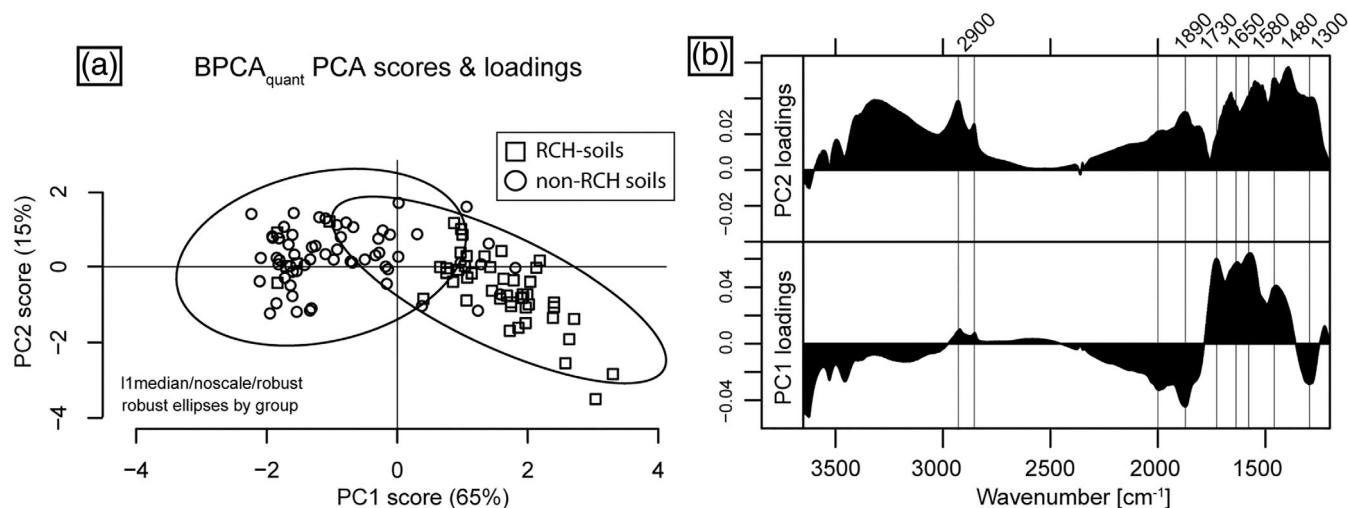

FIGURE 4 (a) Principal component analysis (PCA) score- and (b) loading plots for untreated BPCA$_{quant}$ soil sample spectra. RCH soil: Auh & cu horizons; non-RCH soil: Ahb, Bwb, Ah, Bw and C horizons

(Figure 4a). Figure 4b shows the corresponding PCA loading values, which can be seen as the weights associated with each principle component, giving an idea about which wavenumber regions are influential for the difference in score values. The main separator along PC 1 were negative loadings for wavenumber regions associated with mineral soil components such as clay minerals (approximately 3500 cm^{-1}), SiO$_2$ overtones (Volkov et al., 2021) (peaking at 1890 cm^{-1}), C-O, CH, CH$_2$ vibrations in alkenes and phenolic groups (Hobley et al. 2014) (approximately 1300 cm^{-1})

and positive loadings for the region associated with aromatic carbon C=C and carboxyl C=O (1750 cm^{-1}– 1400 cm^{-1}). Loadings for PC 2 were mainly positive, and the main differences compared to PC 1 were the stronger influence of aliphatic CH and CH$_2$ absorptions at approximately 2900 cm^{-1} and the absence of any influence by carboxylate C=O absorptions at 1740 cm^{-1}. Coincidently, aliphatic CH absorptions at approximately 2900 cm^{-1} were notably less intense in RCH soils (Figure 4). Furthermore, the loadings at absorptions related to C-O, CH, CH2 vibrations in
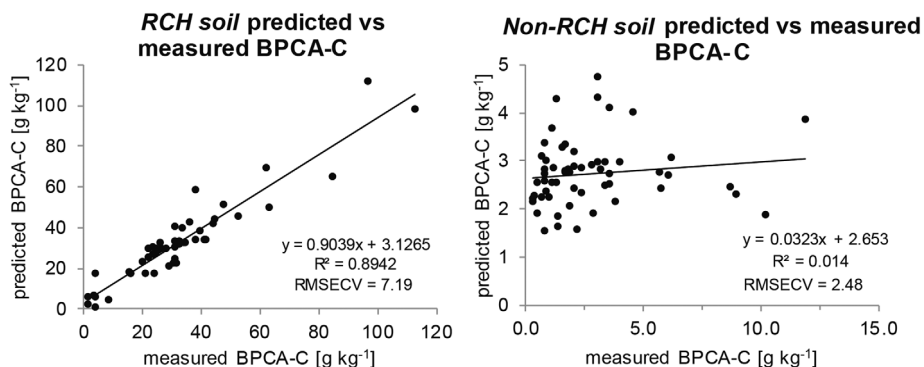
FIGURE 5 PLSR BPCA-C prediction model evaluation using cross-validation for *RCH soil* (Auh & Cu horizons) and *non-RCH soil* (Ahb, Bwb, Ah, Bw, C horizons) BPAC$_{quant}$ spectra
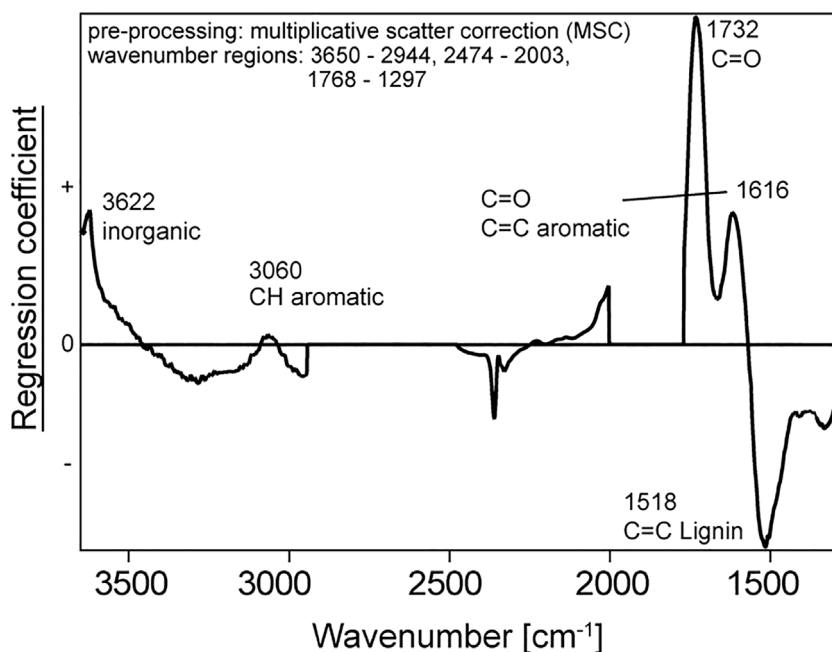
FIGURE 6 PLSR regression coefficient for RCH soil spectra in the BPCA$_{quant}$ dataset

alkenes and phenolic groups (1300 cm^{-1}) were positive in PC 2. The grouping of RCH and non-RCH soil spectra can further be seen in a dendrogram for an exemplary subset of 20 spectra (Figure S2), where most technogenic and reference soil spectra belonged to separate groups. However, the TOC content of the Cu horizons was especially heterogeneous, making some samples more similar to reference spectra, presumably caused by their very low TOC content. We created separate PLSR quantification models for carbon rich Auh and Cu horizons (RCH soils) and reference soils and Cu horizons with low carbon contents (non-RCH soils) to improve the prediction accuracy of BPCA-C concentrations. Cu horizons where included in the calibration dataset of a prediction model based on a threshold of their average TOC content (Table 1), where samples with <38.4 g TOC kg^{-1} are assigned to the non-RCH soil group.

4.3 | PLSR model validation

PLSR predicted BPCA-C concentrations in *RCH soils* very well ($r^2 = 0.89$); however, it failed to predict concentrations for *non-RCH soils* ($r^2 = 0.01$) (Figure 5). The reason for this was the very low TOC and BC concentrations in *non-RCH soils*, which failed to produce a strong enough signal in the spectra. The PLSR regression coefficients for the *RCH soil* model (Figure 6) suggested that higher BPCA-C concentrations coincided with higher carboxyl C=O absorptions at 1732 cm^{-1}, aromatic C=C absorptions from ionised carboxyl (COO^{-}) groups or C=O absorptions at 1616 cm^{-1} (Rebollo et al., 2008; Volkov et al., 2021), aromatic C-H vibrations at 3000–3100 cm^{-1} and lower absorptions at the aliphatic CH region at 2800–3000 cm^{-1} and aromatic C=C stretches associated with lignin at 1518 cm^{-1} (Ferrari et al., 2011; Volkov et al., 2021; White et al., 2011). Thereby, the coefficients
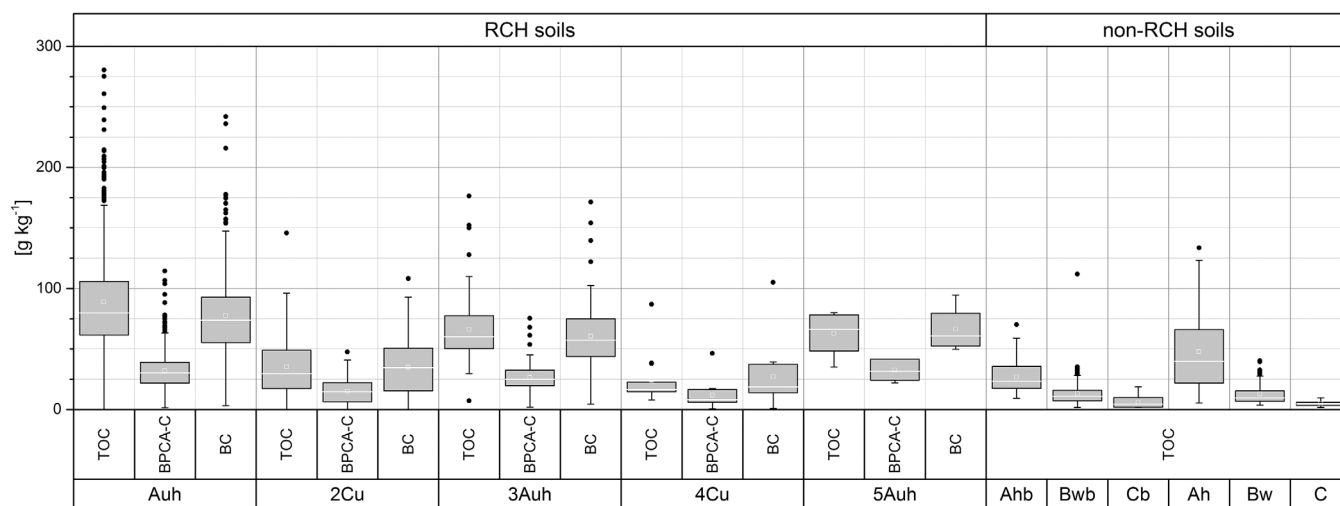
FIGURE 7 Total carbon (TOC), predicted BPCA-derived carbon (BPCA-C) and calculated black carbon (BC) concentrations for RCH soils and non-RCH soil horizons

TABLE 4 Concentrations of measured nitrogen (TN), carbon (TOC), predicted BPCA-derived carbon (BPCA-C) and calculated black carbon (BC) concentrations grouped by soil horizon (mean ± standard deviation) for all samples

|			[g kg⁻¹]				Ratio		
	Horizon	*n*	TN	TOC	BPCA-C	BC	BPCA-C	BC	Avg. C:N
RCH soils	Auh	600	2.4 ± 1.0	89.4 ± 41.0	32.0 ± 14.9	72.6 ± 33.8	0.35	0.85	37.2
	2Cu	131	1.0 ± 0.5	36.1 ± 23.7	15.1 ± 9.8	34.2 ± 22.2	0.41	0.94	36.1
	3Auh	100	1.5 ± 0.4	66.7 ± 26.9	26.7 ± 13.1	60.6 ± 29.7	0.40	0.90	44.4
	4Cu	15	0.7 ± 0.2	27.0 ± 19.8	11.9 ± 12.0	27.0 ± 27.2	0.44	1.00	38.5
	5Auh	12	1.3 ± 0.3	57.8 ± 14.2	29.2 ± 6.6	66.2 ± 14.9	0.50	1.14	44.4
Non-RCH soils	Ah	55	2.5 ± 2.6	50.5 ± 43.5	n.a.				20.2
	Ahb	67	1.0 ± 0.5	26.4 ± 12.5	n.a.				26.4
	Bw	65	0.7 ± 0.3	13.2 ± 8.8	n.a.				18.5
	Bwb	159	0.5 ± 0.3	12.6 ± 7.6	n.a.				25.2
	C	27	0.3 ± 0.1	5.6 ± 3.5	n.a.				18.6
	Cb	14	0.3 ± 0.1	7.1 ± 5.1	n.a.				23.6

Note: The ratio gives the BPCA-C and BC to TOC ratio.

show that BPCA-C concentrations correlated mainly positive with wavenumber regions associated with charcoal contents in soils. Furthermore, inorganic absorptions peaking at 3622 cm⁻¹ were positively correlated with higher BPCA-C concentrations.

Although we separated Cu horizons based on their TOC content for the initial prediction model building, we decided to refrain from this for the further prediction of BPCA-C values, as it would otherwise omit a lot of Cu-horizon spectra from the analysis. This seemed valid, because the measured BPCA-C concentrations for Cu horizons (Table 1) fell within the calibration range of the RCH soil model.

4.4 | Variation in soil carbon concentration by horizon

An overview of the TOC and predicted BPCA-C and BC concentrations for the complete dataset sorted by soil horizons is given in Figure 7, with descriptive statistical values of all soil chemical parameters given in Table 4. The TOC concentration of the Auh horizons was highest in the first Auh and decreased in 3Auh and 5Auh. The Auh horizon had similar BC to TOC ratios as seen for the BPCA$_{quant}$ dataset. Notably, the ratio was increasing for deeper Auh horizons. Outliers with exceptionally high TOC and BC concentrations (up to 281 and 256 g kg⁻¹, respectively) can
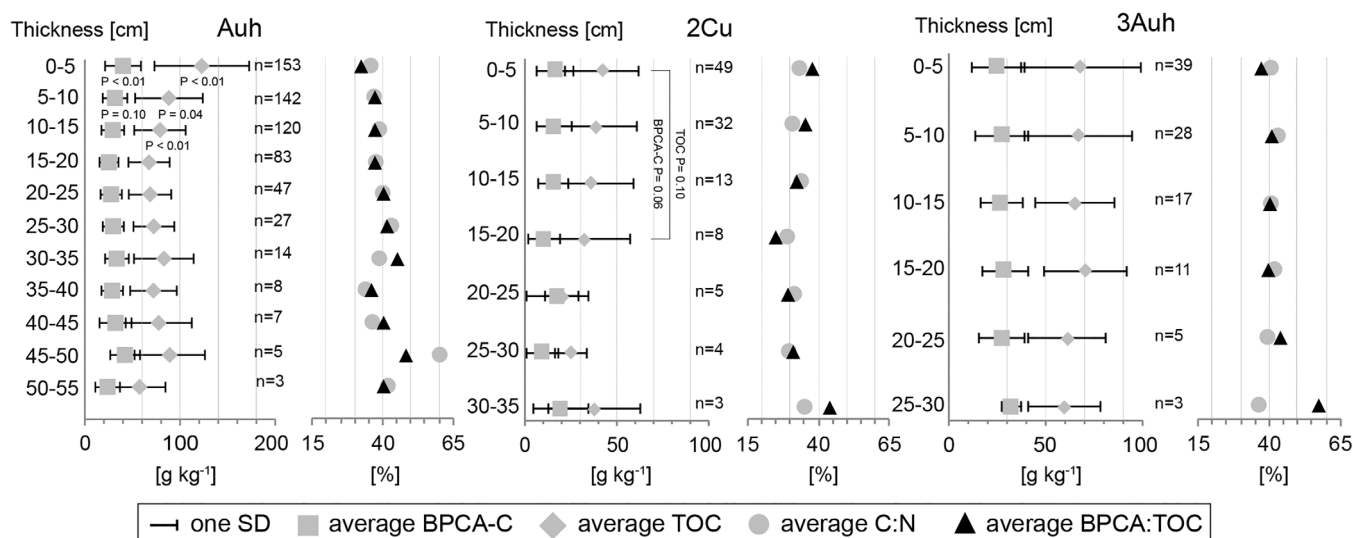
FIGURE 8 Vertical distribution of total carbon and BC carbon concentrations in RCH soil horizons. *p* values from Mann–Whitney U testing are given as a measure for evidence of systematic differences between sampling increments ($p > 0.10$ not shown)

be explained by large contents of charcoal in the respective samples. The 2Cu and 4Cu horizon TOC concentrations were higher than those of reference soils B and C-horizons, suggesting a carbon admixture to the mineral substrate caused by the hearths' operation. Furthermore, the BC to TOC ratios for the 2Cu and 4Cu horizons were higher than those for the BPCA$_{quant}$ dataset. Buried A-horizons and B-horizons featured a lower average TOC concentration than unburied reference soils. The C:N ratios of RCH soils were approximately twice as high as those of non-RCH soils.

4.5 | Vertical distribution of TOC and BPCA-C in RCH soil horizons

The averaged vertical TOC and BPCA-C distribution could only be analysed for Auh, 2Cu and 3Auh horizons, based on the sufficient amount of samples. Depth information (Figure 8) refers to the upper boundary of the horizon, not the ground surface. The Auh horizons contained the highest concentrations of TOC and BPCA-C in the topmost 5 cm, with a decreasing trend until a depth of 20 cm, where they lost 44% of TOC and 31% of BPCA-C. For the first 15 cm to 20 cm depth, there was moderate to strong evidence for a systematic difference between BPCA-C and TOC concentrations at each depth increment ($p \leq 0.1$ and $p < 0.01$). The average BPCA-C:TOC and C:N ratios increased from 32% to 40% and from 36% to 40%, respectively, in the top 30 cm before slightly dropping and fluctuating with increasing depth. The 2Cu-horizon carbon concentrations decreased up to a depth of 25 cm, where they lost 47% of the TOC content and 63% of the BPCA-C concentration. However, evidence for the

first weak to moderate systematic difference between increments was only given when comparing carbon concentrations between depths of 5 and 20 cm ($p = 0.10$ and $p = 0.06$). The BPCA-C:TOC ratio decreased from 38% to 25% in the first 20 cm, while there was no change in the C:N ratio. The 3Auh horizon carbon concentrations showed no vertical trend. The BPCA:C and C:N ratios remained constant until a depth of 20 cm, where they started to diverge. However, the amount of data was very small for depths of 25 and 30 cm.

5 | DISCUSSION

5.1 | Spectra-derived soil properties

Analysing the differences in RCH- and non-RCH soil spectra showed two main results: an interaction of mineral and organic absorption intensities and the increased intensity of carboxyl- and aromatic absorptions in RCH soils, as also described by several studies before. We hypothesise that the difference in spectral properties of RCH and non-RCH soils from the BPCA$_{quant}$ dataset mainly results from the large difference in the TOC quantity and quality of the soil samples. PC 1 (Figure 4) potentially shows the effect that higher absorption intensities from organic soil constituents can have on mineral component absorption intensities, namely, that they lower the latter in the spectra. Conversely, lower absorption intensities related to TOC can result in more pronounced mineral absorptions. This effect can be seen in the spectra (Figure 3), where mineral absorptions at approximately 1900 cm^{-1} are higher in intensity for non-RCH

TABLE 5 Average total organic carbon (TOC) and pyrogenic/highly aromatic carbon (PyC) concentrations for relict charcoal hearth (RCH) topsoil in temperate forests

Study	Methodology	[g kg⁻¹] TOC	PyC	Ratio	Additional OC
Mastrolonardo et al., 2018	Weak nitric acid digestion	129	56	0.43	57%
Mastrolonardo et al., 2019	Walkley-Black digestion	131	65	0.49	51%
Hardy et al., 2019	Differential scanning calorimetry	85	53	0.62	38%
Hardy & Dufey, 2017b	Walkley-Black digestion	106	82	0.77	23%
Abdelrahman et al., 2018	BPCA (×2.27)	111	30	0.27	73%
This study	BPCA (no factor)	89	32	0.35	65%
This study	BPCA (×2.27)	89	72	0.80	20%

Note: The ratio gives the PyC/charcoal-derived C to TOC ratio.

soils than for RCH soils. PC 1 (Figure 4) shows the importance of wavenumber regions associated with carboxyl C=O and aromatic C=C absorptions, which are higher in intensity in RCH soil spectra (Figure 4). This result is further shown by the PLSR regression coefficients for RCH soils (Figure 6), which are mainly sensitive to carboxyl and ionised carboxyl COO⁻ groups. The positive correlation coefficients of absorptions in the phyllosilicate region (3622 cm^{-1}) (Figure 6) cannot be reasonably explained as of now, but could very well be a pseudo-predictor caused by the large amount of variables used by the PLSR model.

The spectral properties suggest an ongoing weathering of charcoal in RCH soils. An increase in carboxylic properties has been described for RCH soils (Hardy et al., 2019) and for incubation experiments where fresh and historic charcoal pieces (19th century) were artificially aged for several months, resulting in an increase in carboxylic groups by the oxidation of carbon compounds on the charcoal surface and interior (Cheng et al., 2008; Cheng et al., 2014). This effect can be increased by introducing non-charcoal biomass to the process (Cheng et al., 2006). Cohen-Ofri et al. (2006) termed this effect the "self-humification" of charcoal, which is further discussed by Ascough et al., 2011. They described the presence of highly carboxylated aromatic humic acids in aged charcoal, which originate, at least in part, from the weathering of the charcoal itself and not from exogenous sources. Furthermore, the less intense aliphatic CH absorptions at approximately 2900 cm^{-1} in RCH soils suggest a lower content of relatively labile carbon compounds compared to reference soils. Similar findings are discussed by Abdelrahman et al. (2018), who reported stronger signals for aliphatic carbon from long chained molecules (e.g., waxes and fatty acids) in NMR spectra of forest soils compared to some RCH soils. We suggest that this could be a direct result of the charcoal burning

process that acts as a reset point for any non-charcoal carbon compounds in the affected soils, since they are most likely charred during the final burning on a site. Compared to the reference soils, the RCH sites then had a relatively short time to accumulate fresh SOM (approximately 120–250 years, Raab et al., 2017), although most SOM has a decadal residence time (Schmidt et al. 2011). Furthermore, other factors that could influence the input and degradation rate of fresh biomass cannot be ruled out, such as changes in vegetation and microbial composition and growth at RCH sites.

5.2 | TOC enrichment of RCH soils

The ratios of PyC to TOC in RCH soils that have been observed in other studies vary strongly, and the variety of methods used to quantify pyrogenic/highly aromatic carbon makes only for a superficial comparison (Table 5).

Additional RCH soil OC contents in RCH soils have been discussed by several studies, although the majority of them studied RCH sites under long-term agricultural use (Burgeon et al., 2020; Hernandez-Soriano et al., 2016; Kerré et al., 2016). The effect is attributed to sorption and consequent sequestration of dissolved organic matter (DOM) on charcoal surfaces (Borchard et al., 2014), whereby a preferential accumulation of hydrophilic, humic-like compounds can take place (Heitkötter & Marschner, 2015; Kerré et al., 2016). Furthermore, charcoal-derived SOM seems to be stabilised through organo-mineral associations in RCH soils (Burgeon et al., 2020), as has been similarly reported for comparably younger biochar-amended soils (Sing & Cowie, 2014; Tilston et al., 2016; Zimmerman et al., 2011). Other studies discuss the absorption of potentially more labile, non-aromatic SOM on charcoal surfaces through vertical transport by DOM (e.g., Wagner et al., 2018).

Since the additions shown in Table 5 are rather large in some cases, other origins should be discussed as well.

Most obviously, methodological uncertainties could be the reason, which could be increased by the specific nature of OC and PyC in RCH. Different quantification methods for PyC can target different parts of the PyC degradation continuum, and as already discussed, RCH substrate seems to be very heterogeneous in its OC and PyC composition. Besides chemical weathering of charcoal, factors influencing its actual production have to be considered. The temperatures within and below charcoal hearths at production have been detected within a relatively wide range (Dupin et al., 2019; Powell et al., 2012), which can result in incomplete charring of SOM and different degrees of aromaticity (Abney et al., 2019; Ascough et al., 2020). Pyrogenic materials with low-order aromaticity caused by degradation (ageing) or lower pyrolysis temperatures at production have been shown to be susceptible to oxidation in laboratory environments (Ascough et al., 2020), that is, they could be overlooked by some PyC quantification methods. Furthermore, the presence and quantity of noncharcoal-related products that potentially remain in the soil as a result of RCH burnings (such as resins, tar and potash) and their resistance to commonly used PyC quantification methods have not yet been studied. Finally, the material that was used to cover the hearth during operation is part of the Auh horizons today and contributes to their TOC. It was most likely a mixture of grass/moss sods, twigs and mineral/topsoil from the adjacent areas and could thereby feature high non-PyC concentrations from the very start.

For the BC quantification method of this study, sources of uncertainty have to be considered. The BPCA-derived carbon in this study can originate from charcoal, aromatic products of the charcoal "self-humification" process and non-charcoal-related aromatic SOM. BPCA markers are used to characterise and quantify organic matrices containing aromatic carbon by splitting up groups of benzene rings and oxidising them, thereby also including nonpyrogenic aromatic carbon (Chang et al., 2018; Kappenberg et al., 2016; Zimmerman & Mitra, 2017). Therefore, the method is reportedly underestimating pyrogenic carbon contents, even for pure charcoal samples, for which ratios of 15% to 26% BPCA-C to TOC have been documented (Hammes et al., 2007; Schneider et al., 2010). Correction factors have been established to convert BPCA-derived carbon into pyrogenic carbon, with a factor of 2.27 given as a conservative estimate for estimating black carbon concentrations in soils (Brodowski et al., 2005). Schneider et al. (2010) discuss that any application of conversion factors adds a potential large source of error in the quantification and that the best solution is to just report measured concentrations as they are. However, interpreting our results in terms of ratios without a correction factor would result in a large difference between TOC and BPCA-C concentrations that could not be explained satisfactorily. Nevertheless, problems arise with factor usage since ratios using corrected BPCA-C often surpass 100% (e.g., Table 3), demonstrating that a fixed correction factor is not universally applicable.

For the results of this study, subtracting BPCA-C from TOC concentrations for the first Auh horizon results in a TOC content similar to that of the reference soil Ah horizon (approximately 50 g TOC kg^{-1}), which suggests that the Auh horizon has started to accumulate fresh SOM. The higher ratios in the 3Auh and 5Auh horizons could be explained by a much lower or missing input rate of fresh SOM and by a higher degree of aromaticity caused by an older age of these horizons compared to the topmost Auh. The same reasoning applies when looking at BC instead of BPCA-C ratios, despite these ratios being much larger, for example, non-BC carbon in the topmost Auh horizons now reaches approximately 17 g TOC kg^{-1} instead of 50 g TOC kg^{-1}. This could also explain the lower absorption intensities of aliphatic carbon spectral features compared to reference Ah horizons. BC ratios of nearly 100% (and above) for the 2Cu, 4Cu and 5Auh horizons suggest that the TOC in deeper horizons is more or less completely made up of highly aromatic carbon.

In summary, the ubiquitously observed increase in TOC contents compared to reference soils is either caused by methodological sources of uncertainty in quantifying PyC, by the specific composition of RCH OC, or by postburn accumulation of SOM; but likely a combination of all factors.

5.3 | Vertical distribution of carbon

Potential vertical translocation processes can best be assessed from the vertical distribution of carbon in the 2Cu horizon (Figure 8) since it consists of relocated mineral substrate and therefore, a homogeneous carbon distribution at the time of its deposition can be assumed. Although, buried topsoils also show higher ratios of BC, again suggesting a vertical translocation of aromatic carbon or a mechanical admixture of charcoal during the hearths operation. We observed a 177% to 544% increase in TOC concentrations for 2Cu horizons compared to non-RCH Bw and C horizons respectively. Thereby, 94% of the TOC is pyrogenic carbon (Table 4). This increase might in part be due to charcoal pieces that are sometimes found in 2Cu horizons of RCHs in the area (Raab et al., 2017), presumably resulting directly from the operation of the hearths

(raking, digging). However, the gradual decrease in TOC concentrations and aromaticity in the first 20 cm of the 2Cu horizons also suggests vertical translocation originating in Auh horizons. Evidence of bioturbation has not been detected in our study area.

Comparable vertical transport of pyrogenic carbon is described for wildfire affected- and biochar amended soils in particulate and soluble form (Bellè et al., 2021; Braun et al., 2020). It remains unclear if these processes are still ongoing in RCH soils. However, the evidence of charcoal degradation described here and in other studies suggest the continuing formation of water extractable black carbon in RCH soils. This could be of interest when studying RCH sites located in areas with occurring podsolisation. If the natural A horizons are replaced by RCH substrate of up to several decimetres in thickness, this would allow to study the effect of increased amounts of soluble aromatic organic acids on buried E horizons.

The vertical TOC distribution in the top 20 cm of the Auh horizon suggest an accumulation of non-pyrogenic carbon. However, based on FTIR spectra analysis as shown in Figure 3 and discussed in section 5.1, the accumulated TOC seems to be of different composition compared to reference topsoils. This could hint at changed SOM turnover dynamics in RCH soils. Mastrolonardo et al. (2019) describe a PyC enrichment for the lower part of RCH substrate for sites in Belgium, which we could not confirm for our sites.

6 | CONCLUSIONS

- The spectral properties of our studied RCH soils suggested an increase in aromatic and carboxylic properties when compared to the SOM of reference soils. This hints at ongoing charcoal degradation processes that potentially resulted in the formation of water extractable aromatic acids.
- The vertical distribution of TOC in topmost Auh horizons suggested an accumulation of recent, non-pyrogenic SOM. However, less intense aliphatic carbon absorptions in RCH soil spectra suggested potentially different SOM turnover dynamics compared to reference soils.
- The ratio of BC contents and TOC contents suggested an accumulation of additional SOM in RCH soils. The origin of this additional SOM seems unclear as of now. It is hypothesised to be a combination of methodological uncertainties when quantifying PyC, a postburn accumulation of SOM, and the potential SOM enriched original RCH cover material.
- The vertical distribution of PyC in 2Cu and Ahb horizons suggested a translocation of aromatic carbon compounds from the Auh horizons into buried mineral soils and the continuing formation of water extractable black carbon even after centuries of charcoal incorporation into the soils.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

ORCID

Alexander Bonhage https://orcid.org/0000-0001-9577-2406
Thomas Raab https://orcid.org/0000-0002-7135-9403
Shaghayegh Ramezany https://orcid.org/0000-0002-4071-7722

REFERENCES

Abdelrahman, H., Hofmann, D., Berns, A. E., Meyer, N., Bol, R., & Borchard, N. (2018). Historical charcoal additions alter water extractable, particulate and bulk soil C composition and stabilization. *Journal of Plant Nutrition and Soil Science*, *181*, 809–817. https://doi.org/10.1002/jpln.201800261

Abney, R. B., & Berhe, A. A. (2018). Pyrogenic carbon erosion: Implications for stock and persistence of pyrogenic carbon in soil. *Frontiers in Earth Science*, *6*, 104127. https://doi.org/10.3389/feart.2018.00026

Abney, R. B., Jin, L., & Berhe, A. A. (2019). Soil properties and combustion temperature: Controls on the decomposition rate of pyrogenic organic matter. *Catena*, *182*, 104127. https://doi.org/10.1016/j.catena.2019.104127

Ascough, P. L., Bird, M. I., Francis, S. M., & Lebl, T. (2011). Alkali extraction of archaeological and geological charcoal: Evidence for diagenetic degradation and formation of humic acids. *Journal of Archaeological Science*, *38*, 69–78. https://doi.org/10.1016/j.jas.2010.08.011

Ascough, P. L., Brock, F., Collinson, M. E., Painter, J. D., Lane, D. W., & Bird, M. (2020). Chemical characteristics of macroscopic pyrogenic carbon following millennial-scale environmental exposure. *Frontiers in Environmental Science*, *7*, 1–15. https://doi.org/10.3389/fenvs.2019.00203

Bellè, S. L., Berhe, A. A., Hagedorn, F., Santin, C., Schiedung, M., van Meerveld, I., & Abvien, S. (2021). Key drivers of pyrogenic carbon redistribution during a simulated rainfall event. *Biogeosciences*, *18*, 1105–1126. https://doi.org/10.5194/bg-18-1105-2021

Bird, M. I., Wynn, J. G., Saiz, G., Wurster, C. M., & McBeath, A. (2015). The pyrogenic carbon cycle. *Annual Review of Earth and Planetary Sciences*, *43*, 273–298. https://doi.org/10.1146/annurev-earth-060614-105038

Bonhage, A., Hirsch, F., Schneider, A., Raab, A., & Raab, T. (2020a). Long term anthropogenic enrichment of soil organic matter stocks in forest soils - detecting a legacy of historical charcoal production. *Forest Ecology and Management*, *459*, 117814. https://doi.org/10.1016/j.foreco.2019.117814

Bonhage, A., Hirsch, F., Raab, T., Schneider, A., Raab, A., & Ouimet, W. (2020b). Characteristics of small anthropogenic landforms resulting from historical charcoal production in western Connecticut, USA. *CATENA*, *195*, 104896. https://doi.org/10.1016/j.catena.2020.104896

Borchard, N., Ladd, B., Eschemann, S., Hegenberg, D., Maria Möseler, B. M., & Amelung, W. (2014). Black carbon and soil properties at historical charcoal production sites in Germany. *Geoderma*, *232*, 236–242. https://doi.org/10.1016/j.geoderma.2014.05.007

Braun, M., Kappenberg, A., Sandhage-Hofmann, A., & Lehndorff, E. (2020). Leachable soil black carbon after biochar application. *Organic Geochemistry*, *143*, 103996. https://doi.org/10.1016/j.orggeochem.2020.103996

Brodowski, S., Rodionow, A., Haumaier, L., Glaser, B., & Amelung, W. (2005). Revised black carbon assessment using benzene polycarboxylic acids. *Organic Geochemistry*, *36*, 1299–1310. https://doi.org/10.1016/j.orggeochem.2005.03.011

Buras, A., Hirsch, F., Schneider, A., Scharnweber, T., van der Maaten, E., Cruz-García, R., Raab, T., & Wilmking, M. (2020). Reduced above-ground growth and wood density but increased wood chemical concentrations of scots pine on relict charcoal hearths. *Science of the Total Environment*, *1*, 137189. https://doi.org/10.1016/j.scitotenv.2020.137189

Burgeon, V., Fouché, J., Leifeld, J., Chenu, C., & Cornélis, J.-T. (2020). Organo-mineral associations largely contribute to the stabilization of century-old pyrogenic organic matter in cropland soils. *Geoderma*, *388*, 114841. https://doi.org/10.1016/j.geoderma.2020.114841

Carrari, E., Ampoorter, E., Bottalico, F., Chirici, G., Coppi, A., Travaglini, D., Verheyen, K., & Selvi, F. (2017). The old charcoal kiln sites in central Italian forest landscapes. *Quaternary International*, *458*, 214–223. https://doi.org/10.1016/j.quaint.2016.10.027

Carrari, E., Ampoorter, E., Bussotti, F., Coppi, A., Nogales, A. G., Pollastrini, M., Verheyen, K., & Selvi, F. (2018). *Effects of charcoal hearth soil on forest regeneration: Evidence from a two-year experiment on tree seedlings*. Manag. https://doi.org/10.1016/j.foreco.2018.05.038

Chang, Z., Tian, L., Li, F., Zhou, Y., Wu, M., Steinberg, C. E. W., Dong, X., Pan, B., & Xing, B. (2018). Benzene polycarboxylic acid - a useful marker for condensed organic matter, but not for only pyrogenic black carbon. *Science of the Total Environment*, *626*, 660–667. https://doi.org/10.1016/j.scitotenv.2018.01.145

Cheng, C. H., Lehmann, J., & Engelhard, M. H. (2008). Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. *Geochimica et Cosmochimica Acta*, *72*, 1598–1610. https://doi.org/10.1016/j.gca.2008.01.010

Cheng, C. H., Lehmann, J., Thies, J. E., Burton, S. D., & Engelhard, M. H. (2006). Oxidation of black carbon by biotic and abiotic processes. *Organic Geochemistry*, *37*, 1477–1488. https://doi.org/10.1016/j.orggeochem.2006.06.022

Cheng, C. H., Lin, T.-P., Lehmann, J., Fang, L. J., Yang, Y.-W., Menyailo, O. V., Chang, K. H., & Lai, J.-S. (2014). Sorption properties for black carbon (wood char) after long term exposure in soils. *Organic Geochemistry*, *70*, 53–61. https://doi.org/10.1016/j.orggeochem.2014.02.013

Cohen-Ofri, I., Weiner, L., Boaretto, E., Mintz, G., & Weiner, S. (2006). Modern and fossil charcoal: Aspects of structure and diagenesis. *Journal of Archaeological Science*, *33*, 428–439. https://doi.org/10.1016/j.jas.2005.08.008

Criscuoli, I., Alberti, G., Baronti, S., Favilli, F., Martinez, C., Calzolari, C., Pusceddu, E., Rumpel, C., Viola, R., & Miglietta, F. (2014). Carbon sequestration and fertility after centennial time scale incorporation of charcoal into soil. *PLoS One*, *9*, e91114. https://doi.org/10.1371/journal.pone.0091114

Dehkordi, R. H., Denis, A., Fouche, J., Burgeon, V., Cornelis, J.-T., Tychon, B., Gomez, E. P., & Meersmans, J. (2020). Remotely-sensed assessment of the impact of century-old biochar on chicory crop growth using high-resolution UAV-based imagery. *International Journal of Applied Earth Observation and Geoinformation*, *91*, 102147. https://doi.org/10.1016/j.jag.2020.102147

Donovan, S., Ignatiadis, M., Ouimet, W., Dethier, D., & Hren, M. (2021). *Gradients of geochemical change in relic charcoal hearths soils*. Catena. https://doi.org/10.1016/j.catena.2020.104991

Dupin, A., Sordoilett, D., Fréville, K., Girardclos, O., & Gauthier, E. (2019). The taphonomic characterization of a charcoal production platform. Contribution of an innovative pair of methods: Raman analysis and micromorphology. *Journal of Archaeological Science*, *107*, 87–99. https://doi.org/10.1016/j.jas.2019.05.003

Ferrari, E., Francioso, O., Nardi, S., Saladini, M., Ferro, N. D., & Morari, F. (2011). DRIFT and HR MAS NMR characterization of humic substances from a soil treated with different organic and mineral fertilizers. *Journal of Molecular Structure*, *998*, 216–224. https://doi.org/10.1016/j.molstruc.2011.05.035

Garcia-Berreda, S., Molina-Grau, S., Forcadell, R., Sánchez, S., & Reyna, S. (2017). Long-term soil alteration in historical charcoal hearths affects tuber melanosporum mycorrhizal development and environmental conditions for fruiting. *Mycorrhiza*, *27*, 603–609. https://doi.org/10.1007/s00572-017-0773-0

Gerke, J. (2018). Concepts and misconceptions of humic substances as the stable part of soil organic matter: A review. *Agronomy*, *8*, 76. https://doi.org/10.3390/agronomy8050076

Gerke, J. (2019). Black (pyrogenic) carbon in soils and waters: A fragile data basis extensively interpreted. *Chemical and Biological Technologies in Agriculture*, *6*, 13. https://doi.org/10.1186/s40538-019-0151-6

Gießelmann, U. C., Borchard, N., Traunspurger, W., & Witte, K. (2019). Long-term effects of charcoal on nematodes and other soil meso- and microfaunal groups at historical kiln-sites – A pilot study. *European Journal of Soil Biology*, *93*, 103095. https://doi.org/10.1016/j.ejsobi.2019.103095

Glaser, B., Haumaier, L., Guggenberger, G., & Zech, W. (1998). Black carbon in soils: The use of benzenecarboxylic acids as

specific markers. *Organic Geochemistry*, *29*, 811–819. https://doi.org/10.1016/S0146-6380(98)00194-6

Hammes, K., Schmidt, M., Smerink, R., Currie, L., Ball, W., Nguyen, T., Louchouarn, P., Houel, S., Gustafsson, Ö., Elmquist, M., Cornelissen, G., Skjemstad, J., Masiello, C., Song, J., Peng, P., Mitra, S., Dunn, J., Hatcher, P., Hockaday, W., ... Ding, L. (2007). Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. *Global Biogeochemical Cylces*, *21*, GB 3016. https://doi.org/10.1029/2006GB002914

Hardy, B., Cornelis, J.-T., Houben, D., Lambert, R., & Dufey, J. E. (2016). *The effect of pre-industrial charcoal kilns on chemical properties of forest soil of Wallonia*. Eur. J. Soil Sci. https://doi.org/10.1111/ejss.12324

Hardy, B., Cornelis, J.-T., Houben, D., Leifeld, J., Lambert, R., & Dufey, J. E. (2017a). *Evaluation of the long-term effect of biochar on properties of temperate agricultural soil at pre-industrial charcoal kiln sites in Wallonia*. Eur. J. Soil Sci. https://doi.org/10.1111/ejss.12395

Hardy, B., & Dufey, J. E. (2017b). The resistance of centennial soil charcoal to the "Walkley-black" oxidation. *Geoderma*, *303*, 37–43. https://doi.org/10.1016/j.geoderma.2017.05.001

Hardy, B., Sleutel, S., Dufey, J. E., & Cornelis, J.-T. (2019). *The long-term effect of biochar on soil microbial abundance*. Frontiers in Environmental Science. https://doi.org/10.3389/fenvs.2019.00110

Heitkötter, J., & Marschner, B. (2015). Interactive effects of biochar ageing in soils related to feedstock, pyrolysis temperature, and historic charcoal production. *Geoderma*, *245-246*, 56–64. https://doi.org/10.1016/j.geoderma.2015.01.012

Hernandez-Soriano, M. C., Kerré, B., Goos, P., Hardy, B., Dufey, J., & Smolders, E. (2016). Long-term effect of biochar on the stabilization of recent carbon: Soils with historical inputs of charcoal. *GCB Bioenergy*, *8*, 371–381. https://doi.org/10.1111/gcbb.12250

Hirsch, F., Raab, T., Ouimet, W., Dethier, D., Schneider, A., & Raab, A. (2018a). Soils on historic charcoal hearths: Terminology and chemical properties. *Soil Science Society of America Journal*, *81*, 1427–1435. https://doi.org/10.2136/sssaj2017.02.0067

Hirsch, F., Schneider, A., Bauriegel, A., Raab, A., & Raab, T. (2018b). *Formation, classification, and properties of soils at two relict charocal hearth sites in Brandenburg*. Front. Environ. Sci. https://doi.org/10.3389/fenvs.2018.00094

Hirsch, F., Schneider, A., Bonhage, A., Raab, A., Drohan, P., & Raab, T. (2020). An initiative for a morphologic-genetic catalog of relict charcoal hearths from Central Europe. *Geoarchaeology*, *35*, 974–983. https://doi.org/10.1002/gea.21799

Hobley, E., Willgoose, G. R., Frisia, S., & Jacobsen, G. (2014). Vertical distribution of charcoal in a sandy soil: evidence from DRIFT spectra and field emission scanning electron microscopy. *European Journal of Soil Science*, *65*(5), 751–762. Portico. https://doi.org/10.1111/ejss.12171

Hobley, E., Zoor, L. C., Shrestha, H. R., Bennett, L. T., Weston, C. J., & Baker, T. G. (2019). Prescribed fire affects the concentration and aromaticity of soluble soil organic matter in forest soils. *Geoderma*, *341*, 138–147. https://doi.org/10.1016/j.geoderma.2019.01.035

IUSS Working Group WRB. (2014). *World Reference Base for soil resources 2014, update 2015* (p. 181). FAO.

Kappenberg, A., Bläsing, M., Lehndorff, E., & Amelung, W. (2016). Black carbon assessment using benzene polycarboxylic acids: Limitations for organic-rich matrices. *Organic Geochemistry*, *94*, 47–51. https://doi.org/10.1016/j.orggeochem.2016.01.009

Kasozi, G. N., Zimmerman, A. R., Nkedi-Kizza, P., & Gao, B. (2010). Catechol and humic acid sorption onto a range of laboratory produced black carbon (biochars). *Environmental Sciene and Technology*, *44*, 6189–6195. https://doi.org/10.1021/es1014423

Kerré, B., Bravo, C. T., Leifeld, J., Cornelissen, G., & Smolders, E. (2016). Historical soil amendment with charcoal increases sequestration of non-charcoal carbon: A comparison among methods of black carbon quantification. *European Journal of Soil Science*, *67*, 324–331. https://doi.org/10.1111/ejss.12338

Kerré, B., Willaert, B., & Smolders, E. (2017). Lower residue decomposition in historically charcoal enriched soils is related to increased adsorption of organic matter. *Soil Biology and Biochemistry*, *104*, 1–7. https://doi.org/10.1016/j.soilbio.2016.10.007

Kurth, V. J., MacKenzie, M. D., & DeLuca, T. H. (2006). Estimating charcoal contents in forest mineral soils. *Geoderma*, *137*, 135–139. https://doi.org/10.1016/j.geoderma.2006.08.003

Lasota, J., Błońska, E., Babiak, T., Piaszczyk, W., Stępniewska, H., Jankowiak, R., Boroń, P., & Boroń, A. L. (2021). *Effect of charcoal on the properties*. Forests. https://doi.org/10.3390/f12111488

Llorente, M., Turrión, M.-B., & Glaser, B. (2018). Rapid and economical quantification of black carbon in soils using a modified benzene polycarboxylic acids (BPCA) method. *Organic Geochemistry*, *115*, 197–204. https://doi.org/10.1016/j.orggeochem.2017.11.005

Mastrolonardo, G., Calderaro, C., Cocozza, C., Hardy, B., Dufey, J., & Cornelis, J.-T. (2019). Long-term effect of charcoal accumulation in hearth soils on tree growth and nutrient cycling. *Frontiers in Environmental Science*, *7*, 51. https://doi.org/10.3389/fenvs.2019.00051

Mastrolonardo, G., Francioso, O., & Certini, G. (2018). Relic charcoal hearth soils: A neglected carbon reservoir. Case study at Marsiliana forest, Central Italy. *Geoderma*, *315*, 88–95. https://doi.org/10.1016/j.geoderma.2017.11.036

Mikan, C. J., & Abrams, M. D. (1995). Altered forest composition and forest development on historic charcoal hearths in southeastern Pennsylvania. *Canadian Journal of Forest Research*, *25*, 687–696. https://doi.org/10.1139/x26-213

Muff, S., Nilsen, E. B., O'Hara, R. B., & Nater, C. R. (2021). Rewriting results sections in the language of evidence. *Trends in Ecology & Evolution*, *37*, 203–210. https://doi.org/10.1016/j.tree.2021.10.009

Powell, A. J., Wheeler, J., & Batt, C. M. (2012). Identifying archaeological wood stack charcoal production sites using geophysical prospection: Magnetic characteristics from a modern wood stack charcoal burn site. *Journal of Archaeological Science*, *39*, 1197–1204. https://doi.org/10.1016/j.jas.2011.11.005

Raab, T., Hirsch, F., Oumiet, W., Johnson, K. M., Dethier, D., & Raab, A. (2017). Architecture of relict charcoal hearths in northwestern Connecticut, USA. *Geoarchaeology*, *32*, 502–510. https://doi.org/10.1002/gea.21614

Rebollo, N. R., Cohen-Ofri, I., Popovitz-Biro, R., Bar-Yosef, O., Meignen, L., Goldberg, P., Weiner, S., & Boaretto, E. (2008).

Structural characterization of charcoal exposed to high and low Ph: Implications for 14C sample preparation and charcoal preservation. *Radiocarbon*, *50*, 289–307. https://doi.org/10.1017/s0033822200033592

Reisser, M., Purves, R. S., Schmidt, M. W. I., & Abvien, S. (2016). Pyrogenic carbon in soils: A literature-based inventory and a global estimation of its content in soil organic carbon and stocks. *Frontiers in Earth Science*, *4*, 80. https://doi.org/10.3389/feart.2016.00080

Robertson, A. H. J., Main, A. M., Robinson, L. J., & Dawson, L. A. (2015). In situ FTIR analysis of soils for forensic applications. *Spectroscopy Supplements*, *30*(8), 22–30.

Schmidt, M. W. I., Skjemstad, J. O., Czimczik, C. I., Glaser, B., Prentice, K. M., Gelinas, Y., & Kuhlbusch, A. J. (2001). Comparative analysis of black carbon in soils. *Global Biogeochemical Cycles*, *15*, 163–167. https://doi.org/10.1029/2000gb001284

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*(7367), 49–56. https://doi.org/10.1038/nature10386

Schneider, A., Hirsch, F., Bonhage, A., Raab, A., & Raab, T. (2020). The soil moisture regime of charcoal-enriched land use legacy sites. *Geoderma*, *366*, 114241. https://doi.org/10.1016/j.geoderma.2020.114241

Schneider, A., Hirsch, F., Raab, A., & Raab, T. (2018). Dye tracer visualization of infiltration patterns in soils on relict charcoal hearths. *Frontiers in Environmental Science*, *6*, 143. https://doi.org/10.3389/fenvs.2018.00143

Schneider, A., Hirsch, F., Raab, A., & Raab, T. (2019). The temperature regime of a charcoal-enriched land use legacy soil. *Soil Science Society of America Journal*, *83*, 565–574. https://doi.org/10.2136/sssaj2018.12.0483

Schneider, M. P. W., Hilf, M., Vogt, U. F., & Schmidt, M. W. I. (2010). The benzene polycarboxylic acid (BPCA) pattern of wood pyrolyzed between 200°C and 1000°C. *Organic Geochemistry*, *41*, 1082–1088. https://doi.org/10.1016/j.orggeochem.2010.07.001

Sing, B. P., & Cowie, A. L. (2014). Long-term influence of biochar on native organic carbon mineralisation in a low-carbon clayey soil. *Scientific Reports*, *4*, 3687. https://doi.org/10.1038/srep03687

Soil Survey Staff. (2014). *Keys to soil taxonomy* (12th ed.). USDA-NRCS.

Stone, J. R., Schafer, J. P., London, E. H., DiGiacomo-Cohen, M. L., Lewis, R. S., & Thompson, W. B. (2005). *Quaternary geologic map of Connecticut and Long Island Sound Basin*. U.S. Geological Survey.

Tilston, E. L., Ascough, P. L., Garnett, M. H., & Bird, M. I. (2016). Quantifying charcoal degradation and negative priming of soil organic matter with a 14C-dead tracer. *Radiocarbon*, *58*, 905–919. https://doi.org/10.1017/rdc.2016.45

Tolksdorf, J. F., Kaiser, K., Petr, L., Herbig, C., Kočár, P., Heinrich, S., Wilke, F. D. H., Theuerkauf, M., Fülling, A., Schubert, M., Schröder, F., Křivánek, R., Schulz, L., Bonhage, A., & Hemker, C. (2020). Past human impact in a mountain forest: Geoarchaeology of a medieval glass production and charcoal hearth site in the Erzgebirge, Germany. *Regional Environmental Change*, *20*, 71. https://doi.org/10.1007/s10113-020-01638-1

Volkov, D., Rogova, O., & Proskurnim, M. (2021). Organic matter and mineral composition of silicate soils: FTIR comparison study by photoacoustic, diffuse reflectance, and attenuated Total reflection modalities. *Agronomy*, *11*, 1879. https://doi.org/10.3390/agronomy11091879

Wagner, T. V., Mouter, A. K., Parsons, J. R., Sevnik, J., van der Plicht, J., & Jansen, B. (2018). Molecular characterization of charcoal to identify adsorbed SOM and assess the effectiveness of common SOM-removing pretreatments prior to radiocarbon dating. *Quaternary Geochronology*, *45*, 74–84. https://doi.org/10.1016/j.quageo.2017.10.006

White, K. E., Reeves, J. B. C., & J., F. (2011). Mid-infrared diffuse reflectance spectroscopy for the rapid analysis of plant root composition. *Geoderma*, *167–168*, 197–203. https://doi.org/10.1016/j.geoderma.2011.08.009

Young, M. J., Johnson, J. E., & Abrams, M. D. (1996). Vegetative and edaphic characteristics on relic charcoal hearths in the Appalachian mountains. *Vegetatio*, *125*, 43–50.

Zimmerman, A. R., Gao, B., & Ahn, M.-Y. (2011). Positive and negative carbon mineralization priming effects among a variety of biochar-amended soils. *Soil Biology and Biochemistry*, *43*, 1169–1179. https://doi.org/10.1016/j.soilbio.2011.02.005

Zimmerman, A. R., & Mitra, S. (2017). Trial by fire: On the terminology and methods used in pyrogenic organic carbon research. *Frontiers in Earth Science*, *5*, 95. https://doi.org/10.3389/feart.2017.00095

SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.