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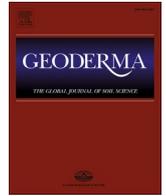
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Quantification of biochar in arable land: A new approach based on Rock-Eval® thermal analysis

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ABSTRACT

Pyrogenic carbon (PyC) constitutes an important pool of soil organic carbon and may remain in soil over millennia. Its accurate quantification in soil is necessary to monitor the evolution of soil carbon stocks and fluxes. This study tested new direct approaches to quantify PyC enrichment in soil, using three protocols based on the Rock-Eval® thermal method. Six industrial biochars and four cultivated soils were mixed at five different biochar/soil ratios from 0.05 % to 1 % (w/w). Biochar-C emissions could be identified in the CO₂ signal from the oxidation stage (CO₂oxi) between 410 °C and 610 °C, independently from carbon and carbonate contents from the original unamended soil. Based on this signal and using a reference sample, the protocol 3 allowed for a good estimation of the PyC enrichment relatively to the reference sample. This protocol is thus well adapted to monitor biochar addition in agricultural soils. However, the use of a reference sample, chosen as the sample with the lowest value of thermo-resistant organic carbon (Corg_{TR}), may be tricky for heterogeneous surface areas and soil profiles. In the latter context, both protocols 1 and 2 are alternative methods to quantify Corg_{TR} from biochar and soil without the need of a reference sample, although less accurate than protocol 3. Protocol 2, based on a more precise identification of the biochar-derived peak of CO₂oxi, resulted in more accurate values than protocol 1. However, the use of protocol 2 is suitable when the biochar-derived peak is easily distinguishable from the peaks derived from both thermo-resistant SOM and PyC present in the original unamended soil. In conclusion, the Rock-Eval® thermal method turns out to be a good tool to quantify biochar-C in cultivated soil and is fully adapted in field experiments – in which, the initial content in biochar is controlled – aiming to decipher the potential benefits of biochar on soil functioning and related ecosystem services.

1. Introduction

Pyrogenic carbon (PyC), the solid residue of the incomplete combustion of organic matter, constitutes a major and persistent pool of the global carbon (C) cycle (Bird et al. 2015). Indeed, PyC globally accounts for around 15 % of soil organic carbon (SOC) (Reisser et al. 2016) and may persist in the environment for millennia (Bowring et al. 2022; Santín et al. 2016; Wang et al. 2016). However, the comprehensive quantification of PyC production as well as its longevity in the environment have so far not been accounted properly in global C budgets (Santín et al. 2015). The low density of PyC and its high concentration,

especially in the top layers of soil after a fire event, may induce its transport away from the site of production by wind and water erosion, followed by redeposition elsewhere (Abney and Berhe 2018; Bellè et al. 2021; Rumpel et al. 2006). Erosion is a significant driver of PyC redistribution and ignoring its role may lead to under- or over-estimation of pyrogenic C mean residence time on the centennial time scale (Abney and Berhe 2018). Recent studies highlighted the need for quantitative understanding of the long-term fate of terrestrial PyC and of PyC fluxes, as both are critical for generating accurate global models of PyC cycling and storage (Abney and Berhe 2018; Bird et al. 2015; Coppola et al. 2022).

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PyC is a part of the black carbon (BC) continuum, as the latter includes the solid material originating from the incomplete combustion of both biomass and fossil fuels (Xie et al. 2024). PyC covers a continuum of chemical composition including charred biomass, charcoal and soot. When intentionally produced for use as a soil amendment and for C sequestration, pyrogenic carbonaceous material is also called biochar (Bird et al. 2015; Lehmann and Joseph 2015). Biochar has been recognized as a negative emission technology (Lehmann 2007; Shrestha et al. 2023; Smith 2016) and may additionally benefit soil fertility and soil agronomic properties (Beusch 2021; Ding et al. 2016; Schmidt et al. 2021). Quantifying biochar thus appears as essential to improve our understanding of its long-term effects for food production.

Many different techniques are currently being used to measure biochar-C concentration in soil. Benzene polycarboxylic acids (BPCA) is a well-established method to quantify PyC in soil and sediment, based on the quantification of molecular markers (Brodowski et al. 2005; Glaser et al. 1998; Llorente et al. 2018; Schneider et al. 2011). However, the sample pre-processing required by this method is time-consuming and may not quantitatively recover the largest and most condensed PyC components (Hammes et al. 2007). Furthermore, BPCAs may not originate only from PyC, but may be produced from uncharred organic matter (OM) (Kappenberg et al. 2016). Alternative methods for PyC or biochar quantification in soils are based on chemical, optical or thermal characteristics (Poot et al. 2009; Xie et al. 2024). However, chemical oxidation process is time-consuming and may induce the loss of PyC particles during the manipulation in liquid solutions (Song et al. 2002). Optical methods are limited by luminosity and uniformity of uncharred organic material, it may identify only specific sized of charred particles and, for the infrared spectroscopy, require extensive data specific to the test region (Bornemann et al. 2008; Han et al. 2007; Khan et al. 2009). Thermal oxidation methods may require values from pure biochar and pure soil and may overestimate BC due to overlapping with signals from soil and uncharred organic carbon with aromatic structure (Hardy et al. 2017; Leifeld 2007). Indeed, BC presents a specific thermal oxidation signature characterized by heat peaks above 350 °C, due to its higher oxidative stability compared to uncharred material (Leifeld 2007). The peaks from BC may interfere with peaks from uncharred soil organic matter (SOM) sharing similar chemical structures and properties of biochar, such as high C content and aromaticity (La Rosa Arranz et al. 2009). Therefore, it can be difficult to identify of a cut-off temperature to differentiate quantitatively between PyC and uncharred SOM (Hardy et al. 2022).

The thermal methods used for BC quantification mainly consist of thermal oxidations (Xie et al. 2024). An additional pyrolysis stage, preceding the oxidation stage, may remove part of uncharred organic carbon (Cadle and Groblicki 1982) and hence, reduce the potential for overlaps between PyC and uncharred SOC. The Rock-Eval® thermal method precisely consist of consecutive pyrolysis and oxidation stages, performed separately in two different ovens and under a progressive increase in temperature, during which carbon emissions through hydrocarbon, CO and CO₂, are measured continuously (Behar et al. 2001; Lafargue et al. 1998). This method was shown to be adaptable to SOM characterisation (Disnar et al. 2003) and appears as particularly powerful to characterize BC, since it can detect a larger part of the BC combustion continuum when compared to other methods (Poot et al. 2009). In addition, thermal analysis has the advantage of being a direct method, without any pre-treatments required (Xie et al. 2024). Although the Rock-Eval® method has been used to characterize BC in sediments (Oen et al. 2006; Poot et al. 2009), it has not yet been used to quantify PyC enrichment in soil.

In this study, we propose new approaches to quantify biochar in soil, using the Rock-Eval® thermal method. Our aims were (i) to identify the signal and temperature range of preferential biochar-C emissions during the Rock-Eval® thermal analysis, (ii) to quantify thermally resistant organic compound, including both PyC and uncharred SOC originally contained in the unamended soil as well as the biochar-C enrichment,

and (iii) to quantify in particular the biochar-C enrichment in biochar-soil mixtures. To do so, we mixed soils from four agricultural fields and biochars from six biomass feedstocks produced by industrial processes, using different biochar/soil ratios. We tested two protocols to quantify thermos-resistant organic compound and one protocol to quantify biochar-C enrichment in the biochar-soil mixtures.

2. Material and method

2.1. Soils, biochars and their mixtures

Four soils (A, B, C and D) were sampled from the top layer (0–30 cm) of fields in the vicinity of Toulouse (France) and Beauvais (France). These soils were selected because of their marked differences in carbon content and in physico-chemical properties. Total organic and mineral C contents (respectively TOC and MINC, measured with the Rock-Eval®), pH_{H2O} and texture of the soils are presented in Table 1. Following the World Reference Base for soils (IUSS Working Group, W.R.B 2015), soil A correspond to a acidic loamy luvisol developed on fluvic material, soil B to a haplic loamy luvisol developed on calcareous loess, soil C to a clayey calcareous cambisol that evolved from limestone and soil D is an acidic loamy cambisol developed over schist and particularly rich in organic matter. These four soils are cultivated with cereals and to the best of our knowledge have not received any intentional input of biochar. Six biochars were made from initial vegetal biomass: herbaceous (Hydroplanete, 78,310 Maurepas, France), maize, miscanthus, rapeseed, compost refusal and wood granula, and were pyrolyzed between 400 °C and 650 °C for 10 min, which are common temperatures for the production of biochar (Lévesque et al. 2022), using an industrial pyrolysis reactor (Biogreen® Pyrolysis Technology, ETIA, Oise, France). Pyrolysis temperature of biochar production (before analysis with the Rock-Eval®) and total organic and mineral C content (TOC and MINC, measured with the Rock-Eval®) of the biochars are presented in Table 2.

To compare the quantification of biochar-derived C from biochar-soil mixtures differing by their soil, the herbaceous biochar was mixed with each of the four soils. Then, to compare the quantification of biochar-derived C from biochar-soil mixtures differing by their biochar, the soil A was mixed with each of the six biochars. For each type of biochar-soil mixture, five biochar/soil ratios (w/w) were used: 0.05 %, 0.10 %, 0.20 %, 0.50 % and 1.00 %.

2.2. Rock-Eval® thermal analysis

All pure soil, biochar and mixtures were analysed with a Rock-Eval® 6 device (Vinci Technologies), at IFP Energies Nouvelles (IFPEN, 92,500 Rueil-Malmaison, France). About 80 mg of dry powdered sample, for each sample, were weighed in steel pots. The analytical protocol included two successive phases, occurring in two different ovens: a pyrolysis phase in an inert N₂ atmosphere at temperatures from 200 °C to 650 °C with a heating rate of 25 °C min⁻¹, and an oxidation phase in an artificial atmosphere (N₂/O₂: 80/20) at temperatures from 200 °C to 850 °C with a heating rate of 25 °C min⁻¹. During the thermal process, hydrocarbon rate from the outgoing flow was measured using a flame

Table 1

Organic and mineral C contents (TOC and MINC), pH_{H2O} and granulometric composition of soils.

Soil	TOC	MINC	pH _{H2O} ¹	Clay ²	Silt ²	Sand ²
	g kg ⁻¹					
A	6.2	0.7	6.6	125	587	288
B	8.2	1.8	8.1	212	736	52
C	7.4	16.8	8.3	334	314	352
D	55.9	4.8	5.9	226	541	233

¹ ISO 10390 norm.

² X 31-107 norm.

Table 2

Temperature (T) of pyrolysis of biochars production and total organic and mineral C content (TOC and MINC) of biochars.

Biochar	Pyrolysis T °C	TOC g kg ⁻¹	MINC g kg ⁻¹
Herbaceous	400	790.0	17.2
Maize	450	644.6	15.1
Compost	450	560.8	19.8
Miscanthus	550	755.6	9.2
Wood	550	777.5	14.4
Rapeseed	650	622.6	35.0

ionization detector, while the CO and CO₂ evolved were measured with infra-red detector (Lafargue et al. 1998). Standard parameters, namely total organic carbon (TOC), mineral carbon (MINC), total carbon (TC=TOC+MINC), hydrogen index (HI) and oxygen index (OI), were calculated by integrating the amounts of hydrocarbons, CO and CO₂ produced during the thermal analysis between defined temperature limits (Behar et al. 2001; Lafargue et al. 1998). HI and OI are both calculated from C emissions during the pyrolysis stage; HI corresponds to the proportion of hydrocarbons to TOC and OI corresponds to the proportion of CO₂ emitted between 200 and 400 °C at the pyrolysis stage to TOC (Table 3) (Behar et al. 2001).

2.3. Quantification of thermo-resistant organic C and biochar-C enrichment

The real biochar-C content in the mixtures (Real biochar-C, in mg C g⁻¹), was quantified using the biochar/carbon ratio, calculated from the mass of biochar and soil in the mixtures (respectively m_{biochar} and m_{soil}, in g) and the total carbon content from biochar (TC_{biochar}, in wt. %), as given by Eq. 1.

$$\text{Real biochar-C} = \frac{m_{\text{biochar}}}{(m_{\text{soil}} + m_{\text{biochar}})} * \text{TC}_{\text{biochar}} * 10 \quad (1)$$

Biochar-C was mainly emitted during the oxidation stage and the CO₂ (CO₂oxi) represented higher quantities than CO during oxidation (COoxi) (Fig. 1, Supplementary Fig. S1, Table S1). To estimate the variations of CO₂oxi emissions induced by the presence of biochar, we calculated the standard deviation of CO₂oxi emissions at each temperature among all biochar/soil ratios for each type of biochar-soil mixture. The standard deviations of CO₂oxi emissions evidenced that biochar-C was mainly emitted between 410 and 610 °C (Fig. 2). Based on CO₂oxi emissions, we tested two protocols (protocols 1 and 2) to quantify the thermo-resistant organic C fraction (Corg_{TR}), including biochar-C enrichment, PyC from the original unamended soil and thermo-resistant uncharred SOC. We also tested a third protocol (protocol 3) to quantify the biochar-C enrichment in the biochar-soil mixtures.

Protocol 1: The first protocol consisted of quantifying Corg_{TR} from the mixture, as the CO₂oxi emitted between 410 and 610 °C.

Protocol 2: In some cases, biochar-C can be emitted in narrower temperature intervals than 410–610 °C. The identification of the specific CO₂oxi peak attributed to biochar allows selecting the temperature interval at which biochar was mainly emitted and hence reduce the part from the soil in the quantification of Corg_{TR}. The second protocol consisted of quantifying Corg_{TR} from the mixtures, as the CO₂oxi emitted between during the narrower temperature intervals than 410–610 °C.

Table 3

Calculated parameter from the Rock-Eval® (Behar et al. 2001). HCpyr: hydrocarbon emitted during the pyrolysis stage. CO₂pyr₂₀₀₋₄₀₀: CO₂ emitted between 200 and 400 °C during the pyrolysis stage.

Name	Unit	Formula	Full name
HI	g HC kg TOC ⁻¹	HCpyr × 100/TOC	Hydrogen index
OI	g CO ₂ kg TOC ⁻¹	CO ₂ pyr ₂₀₀₋₄₀₀ × 100/TOC	Oxygen index

We called Corg_{TR}-peak the result of the Corg_{TR} quantification with this protocol. To specify the temperature intervals of the peak attributed to biochar-C emission, we selected the temperatures at which the standard deviation for all biochar/soil ratios at each biochar-soil mixture was greater than 3×10^{-3} mg C/g (Fig. 2). The limit of 3×10^{-3} mg C/g was chosen arbitrarily.

Protocol 3: To remove the part from SOM in the quantification of Corg_{TR}, and hence, to measure only the part from the biochar in the quantification of Corg_{TR} (char-Corg_{TR}), the third protocol consisted of subtracting the Corg_{TR} from a reference sample, to the Corg_{TR} from the biochar-soil mixture (Supplementary, Fig. S2) and to multiply the value by the empirical correction of 1.35. The reference sample was chosen as soil without biochar added or as the sample with the lowest value of Corg_{TR}. In the case of this study, we used pure soil as reference sample. Hence, char-Corg_{TR} represents the enrichment of Corg_{TR} due to biochar addition, relatively to the reference sample.

We used R version 4.3.3 (R Core Team 2024) for the data analysis.

2.4. Additional data for comparison

To explore the composition of the mixtures, we analysed lignin extracted using the Organosolv process (Johansson et al. 1987) (Sigma-Aldrich, USA). TOC of lignin was 588.6 mg C/g.

We compared results from the biochar-soil mixtures with results from soils where no biochar had been added, using natural soils from Alpine areas that have been studied by (Matteodo et al. 2018).

We compared the added biochar-C quantification from the third protocol using Rock-Eval®, with anthrosols from Isla del Tesoro (Bolivia), where charcoal-C was quantified using the BPCA method (Lombardo et al. 2013).

3. Results

3.1. Rock-Eval® standard parameters

HI and OI of all samples ranged respectively between 0 and 200 g HC kg TOC⁻¹ and between 0 and 300 g CO₂ kg TOC⁻¹. The values of HI and OI from biochars were lower than from soils and biochar-soil mixtures, as they ranged respectively below 25 g HC kg TOC⁻¹ and below 50 g CO₂ kg TOC⁻¹. The values of HI and OI from the mixtures decreased along with corresponding increase of the biochar/soil ratios and stood out from the trend formed by the natural soils (Fig. 3).

3.2. Thermograms

Unlike for the emissions of hydrocarbons, CO and CO₂ from the pyrolysis stage (HCpyr, COpyr and CO₂pyr), the addition of biochar in soil induced a specific peak in the thermograms of both CO and CO₂ emitted during the oxidation stage (COoxi and CO₂oxi) (Fig. 1, Supplementary Fig. S3). CO₂oxi systematically recorded the highest contribution of the total carbon (TC), between 63.6 and 88.0 % TC (Supplementary Table S1). The standard deviations from biochar and biochar-soil mixtures revealed that biochar-C was mainly emitted between 410 and 610 °C (Fig. 2, Supplementary Fig. S1). The presence of carbonaceous material in soil C was revealed by CO₂oxi emissions above 650 °C and did not affect the biochar-C emissions (Supplementary Fig. S3). When added to soil, the peak temperature of biochar-C remained between 410 and 610 °C (Supplementary Fig. S4). Carbon from pure lignin was mainly emitted as HCpyr (49 % TOC) and CO₂oxi (25 % TOC) (Supplementary Table S1) and the CO₂oxi peak occurred between 410 and 610 °C, with a maximum at 539 °C (Supplementary Fig. S5).

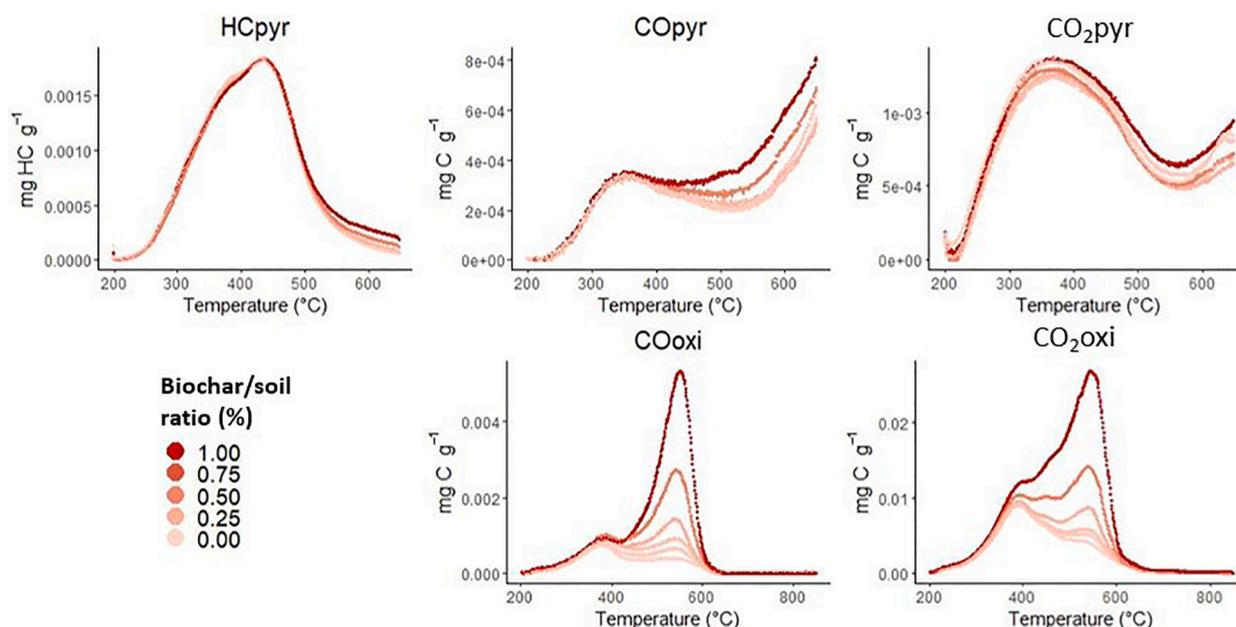


Fig. 1. Hydrocarbon (HC), CO and CO₂ emissions during pyrolysis (pyr) and oxidation (oxi) stages of Rock-Eval® analysis of the mixture with herbaceous biochar and soil A. Thermograms from all other soils, biochar and mixtures are presented in Supplementary, Fig. S3.

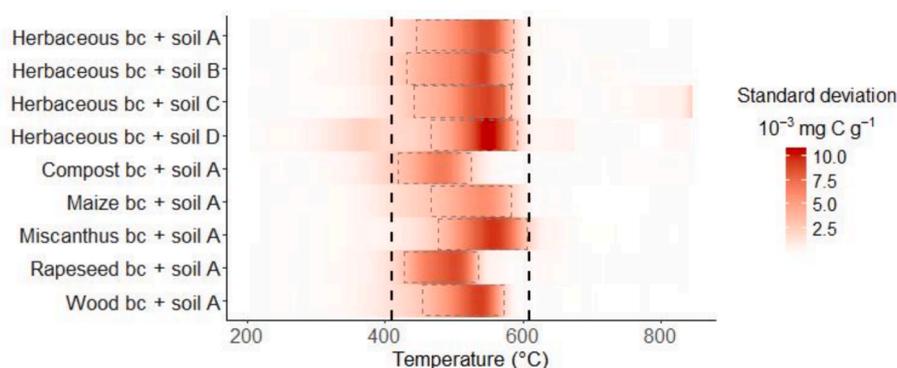


Fig. 2. Standard deviation of CO₂ emissions during the oxidation stage of the Rock-Eval® analysis (CO₂oxi) of all biochar/soil ratios for each type of biochar-soil mixture and each temperature. bc: biochar. The dashed rectangles identify the temperature intervals where the standard deviation is greater than 3×10^{-3} mg C/g.

3.3. Quantification of thermo-resistant organic C and biochar-C enrichment

Biochar-C was quantified in the mixtures using three protocols based on the CO₂oxi emissions from Rock-Eval®. When quantified as the CO₂oxi emitted between 410 and 610 °C (protocol 1) (Fig. 4a) or over a narrower temperature interval (protocol 2) (Fig. 4b), biochar-C was overestimated for the low biochar-C content in all biochar-soil mixtures (<4 mg C/g) and largely overestimated for the herbaceous biochar-soil D mixture. The soil D was the soil with the highest value of TOC as compared to the other soils (Table 1). The overestimation of the biochar-C content in the herbaceous biochar-soil D mixture was higher in the results from Corg_{TR} (protocol 1) than from Corg_{TR-peak} (protocol 2), as it presented biochar-C values respectively about 20 times and 7 times higher than the real values of biochar-C. Biochar-C quantity was slightly underestimated for values above 4 mg C/g by the protocol 2 (Fig. 4b).

To reduce the uncertainties due to overlapping between C emissions from SOM and the added biochar, the protocol 3 quantified char-C by subtracting Corg_{TR} from SOM to Corg_{TR} from the mixture, using a reference sample with the lowest value of Corg_{TR} for each type of biochar-soil mixture. Results from protocol 3 presented a good correlation between estimated and real quantities of biochar-C over all

biochar-soil mixtures ($R^2 = 0.99$) (Fig. 4c).

The protocol 3 was compared to the BPCA method on a soil profile from an anthrosol in Isla del Tesoro (Bolivia) (Lombardo et al. 2013). The reference sample was chosen as the sample with the lowest value of Corg_{TR} in the soil profile, at 60 cm depth. The values of char-Corg_{TR} quantification thus correspond to PyC enrichment relatively to this reference sample. As well, the values of PyC using the BPCA method were calculated as the PyC enrichment as compared to the sample with the lowest value of PyC, according to the results from BPCA (at 50 cm depth). Both BPCA and Rock-Eval® methods yielded similar results all along the soil profile, ranging between 0 and 10 g C kg⁻¹, and with the highest values recorded in the top layers (Fig. 5).

4. Discussion

The aim of the study was to quantify PyC in soil, using the Rock-Eval® thermal method. HI and OI are standard parameters calculated as the part of TOC emitted as hydrocarbons and CO₂ during the pyrolysis stage of the Rock-Eval® analysis (Behar et al. 2001). Values of both HI and OI decreased along with increasing biochar enrichment in the biochar-soil mixtures. The low values of HI and OI from pure biochar is related to its high carbon content and aromaticity, resulting to lower

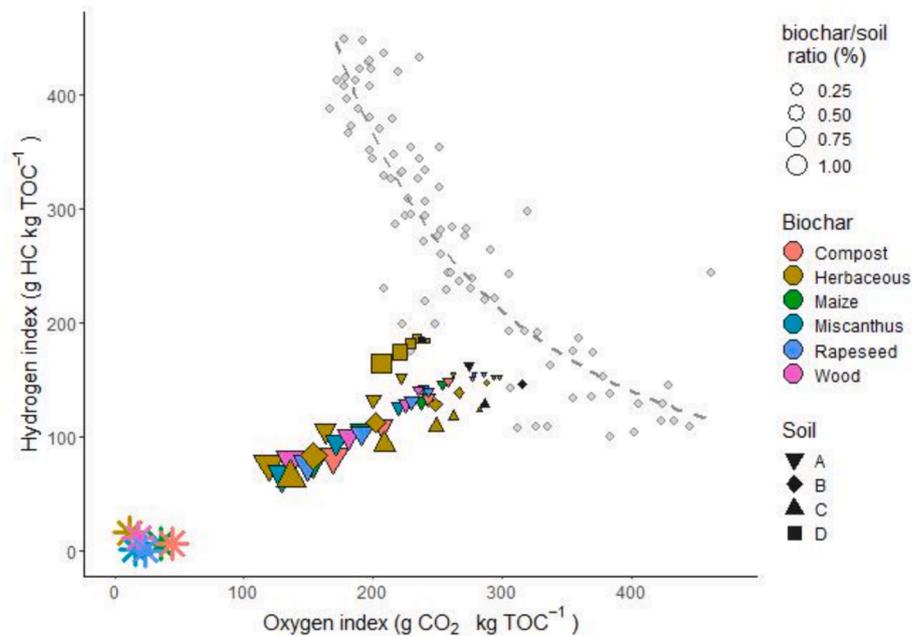


Fig. 3. HI and OI correlations of the biochars (star points), the soils and their mixtures. The grey points represent natural soils where no biochar was added (Matteodo et al. 2018).

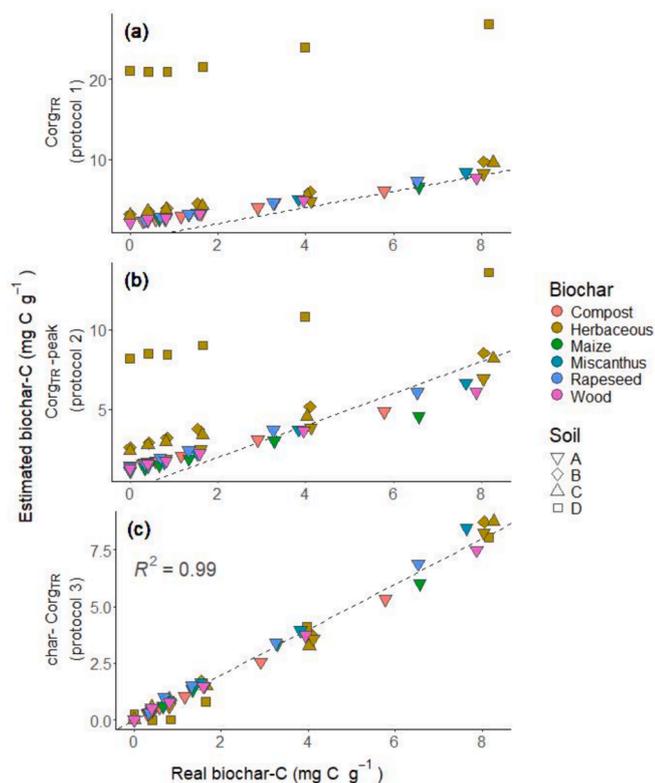


Fig. 4. Correlation between estimated and real C-biochar content in biochar-soil mixtures, using the three protocols for biochar-C quantification: C_{orgTR} from protocol 1, between 410 and 610 °C (a), $C_{orgTR-peak}$ from protocol 2, at the narrower temperature intervals (b) and $char-C_{orgTR}$ from protocol 3, between 410 and 610 °C and with subtraction of C_{orgTR} from the reference sample, i.e. from the sample with the lowest value of C_{orgTR} for each type of biochar-soil mixture (c). The dashed line represents $y = x$.

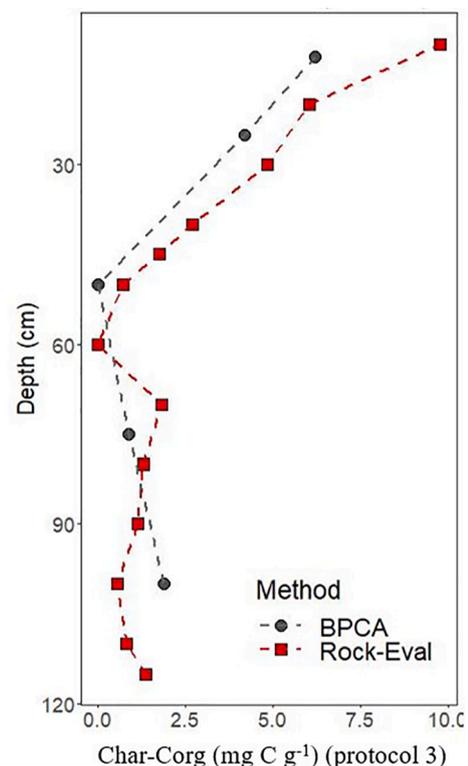


Fig. 5. Comparison of the quantification methods from Rock-Eval® and from benzene polycarboxylic acid (BPCA) to evaluate PyC enrichment in anthrosol from Isla del Tesoro (Bolivia) using the reference sample with the lowest value of C_{orgTR} from the soil profile. The values from the BPCA method are taken from (Lombardo et al. 2013).

hydrogen and oxygen contents as compared to soil (Lehmann and Joseph 2015). The deviation of HI and OI from the mixtures to the trend from natural soils may thus inform about the relative enrichment of biochar in biochar-soil mixtures where both biochar and soil have

known values of HI and OI. Lower values of HI and OI as compared to the natural soils may inform about a relatively higher quantity of charred material, such as PyC from the soil or biochar-C enrichment. However, analysis of the thermograms from the Rock-Eval® evidenced that, within the biochar-soil mixtures, biochar-C was mostly emitted during the oxidation stage. The absence of major effect on C emissions from the pyrolysis stage results from the fact that biochar has already been subjected to pyrolysis during its production. Hence, values from HI and OI may not be the most suitable for accurately quantifying biochar-C in soil.

During the oxidation stage, biochar-C was mostly emitted above 400 °C while uncharred SOM was mostly emitted below 400 °C, consistently with other studies (Hardy et al. 2017; Leifeld 2007). The higher thermal stability of biochar, as compared to uncharred SOM, may result from its higher aromaticity (Lehmann and Joseph 2015; Leifeld 2007). Biochar-C was emitted between 410 and 610 °C during the oxidation stage. The biochars from our study originated from plant biomasses including maize, miscanthus, rapeseed, compost, wood and herbaceous, all containing lignin in different proportions (Kim et al. 2012; Schittenhelm 2008; Tofanica et al. 2011). Since the lignin induced a peak in the same range of temperatures than biochars, we assume that the thermal signature of biochar may be driven by its content of thermally resistant organic aromatic moieties, such as lignin. Furthermore, PyC and uncharred thermo-resistant organic C in the original unamended soils also induced CO₂oxi emissions between 410 and 610 °C, although in smaller quantities than from biochar. The CO₂oxi emissions from both biochar and soils induced overlaps between 410 and 610 °C, as observed in previous studies (Hardy et al. 2017; Hardy et al. 2022). However, the CO₂oxi peaks from biochar remained in the temperature limits of 410 and 610 °C, independently to its blending with soil. Furthermore, the presence of high C content (>60 g kg⁻¹) and carbonates in soil did not affect the biochar-C emissions from the biochar-soil mixtures.

In this study, we tested three different approaches to quantify PyC in soil, based on the CO₂ emissions during the oxidation stage (CO₂oxi) of the Rock-Eval® thermal analysis. The CO₂oxi emissions between 410 and 610 °C from the Rock-Eval® thermal analysis enabled an accurate quantification of the biochar-C enrichment in all biochar-soil mixtures, independently from the SOC and carbonates content from the original unamended soils (protocol 3). The use of the empirical correction of 1.35 for the biochar-Corg_{TR} calculation can be explained by the fact that the CO₂oxi-C emission represents between 63.6 and 88.0 % of the TC. However, this protocol requires the thermogram of a reference sample, and the quantification of PyC enrichment is relative to this reference. In this study, the PyC enrichment corresponded to the biochar-C amendment. The reference sample is ideally chosen as the unamended soil, but when unamended soil is not available, it can be chosen as the sample with the lowest value of Corg_{TR}. In both cases, the reference sample may well contain uncharred thermo-resistant SOM and PyC from the original unamended soil. However, the use of a reference sample can be a source of limitations for the use of this protocol 3. Indeed, thermal properties of SOM may be heterogeneous over a surface area and soil depth, potentially influencing the representativity of the reference sample over a whole surface area or soil profile. This protocol is therefore preferentially adapted to homogeneous surface areas and soil profiles, such as top layers from agricultural soils. For instance, this protocol could be used for tracing dispersion of added biochar or its entrance into specific soil fractions of an agricultural soil. Precautions must be taken when comparing different soil profiles using different reference samples; in this case, the reference samples must be compared with each other, previously to the comparison of all the soil profiles.

In the cases of heterogeneous areas or soil profiles, it is particularly difficult to distinguish between thermo-resistant organic C from the original unamended soil and from the amended biochar. The presence of a CO₂oxi peak between 410 and 610 °C informs about the presence of thermo-resistant organic C, but not about its main source, as it can originate from biochar-C enrichment, PyC from the original unamended

soil or from thermo-resistant uncharred SOC such as ligneous components. However, the presence of an enrichment with charred material can be evidenced by lower values of HI and OI, when compared with values from natural soils. We tested two protocols to quantify thermo-resistant organic C (Corg_{TR}) from the mixture, based on the CO₂oxi emissions and using the broader temperature interval of 410–610 °C (protocols 1) or using narrower temperature interval (protocol 2). Results from both protocols overestimated the biochar-C enrichment, especially in the mixtures with TOC-enriched soil D (55.9 g C kg⁻¹) and with low biochar-C content (<4 mg C/g). These overestimations were largely induced by the overlapping between CO₂oxi emissions from soil and biochar, as observed in previous thermal studies (Hardy et al. 2017). The reduction of the part of C quantification related to CO₂oxi emissions from soil, possible through the identification of a narrower temperature interval of the peak-derived biochar-C in the biochar-soil mixtures (protocol 2), led to a reduction of these overestimations. The protocol 2 can be used when the CO₂oxi peak generated by biochar-C between 410 and 610 °C can be identified and easily distinguishable from the soil matrix. But in the cases where the initial unamended soil is enriched with thermo-resistant uncharred SOC or PyC, the overlapping with biochar-C can making it difficult to identify a specific peak derived from biochar-C. In these cases, the protocol 1 seems more suitable. Both protocols 1 and 2 have the advantage to be applicable for heterogeneous surface areas and soil profiles, since they do not require any reference sample. They may in return result in lower accurate estimations of biochar-Corg_{TR} than protocol 3.

Beyond surface and depth heterogeneities, thermal properties of soil and PyC may also change through time. In particular, despite its ability to remain in soils over centuries (Lehmann and Joseph 2015), biochar is subjected to physical, chemical and biological weathering through time (La Rosa et al. 2018; Spokas et al. 2014; Wang et al. 2020). Biochars degradation start with the mineralization of the labile C pool (<60 days) (Ameloot et al. 2013), and goes on with the breakdown of its recalcitrant aromatic moieties through oxidation (Mia et al. 2017). As the thermal stability of SOM may be closely linked biogeochemical stability (Gregorich et al. 2015; Plante et al. 2011), the decrease of chemical and biological stability of biochar through time may lead to a reduction of its thermal stability (Hardy et al. 2022), thereby leading to more overlapping between PyC and uncharred SOM. To investigate the effects of PyC weathering on the accuracy of its quantification in soil using the Rock-Eval® method, we compared the protocol 3 based on the Rock-Eval® thermal analysis with the BPCA method, on samples from soil profile taken from an anthrosol from Isla del Tesoro in Bolivia. This anthrosols corresponds to a *Terra Preta de Indio* located in the Bolivian Amazon and known as one of the oldest site in the western Amazonia, where people from early-Holocene already started to amend their soil with charcoal (Lombardo et al. 2013). The similar estimations of PyC enrichment from both methods along the soil profile evidenced that the weathering processes did not interfere more with the protocol based on the Rock-Eval® than with the BPCA method for the quantification of PyC enrichment. Hence, the protocol of PyC quantification using the Rock-Eval® method may be used for long-term monitoring of PyC degradation. However, further studies about the effects of weathering on PyC thermal properties would be needed to confirm the negligible effects of weathering on the protocols of PyC quantification.

5. Conclusions

We tested three protocols to quantify biochar-C in controlled biochar-soil mixtures from six industrial plant-derived biochars and four cultivated soils, based on the CO₂oxi emissions (oxidation stage) from Rock-Eval® thermal analysis. Biochar-C could be identified through the CO₂oxi peak between 410 °C and 610 °C, independently from C and carbonaceous contents from the original unamended soil. Based on this signal, the protocol 3 provided good estimations of the biochar-C enrichment relatively to a reference sample, chosen as the sample

with the lowest value of thermo-resistant organic carbon (Corg_{TR}). This protocol 3 is thus well adapted to relatively homogenous surface areas and profiles, such as top layers from agricultural soils. Applications can be the monitoring of added biochar into bulk soil or specific soil fractions. However, the use of a reference sample may be tricky when quantifying PyC enrichment in very heterogeneous surface areas or soil profiles. For the latter cases, the two protocols (protocols 1 and 2) consisted in quantifying Corg_{TR} from the biochar-soil mixtures, independently from the original source of the Corg_{TR}. Indeed, Corg_{TR} may originate from thermo-resistant SOM, PyC from the original unamended soil and PyC from added organic amendment such as biochar. These two alternative protocols were however less accurate than the protocol 3 to quantify biochar-C enrichment. The protocol 2 consisted in quantifying the total amount of Corg_{TR} between 410 °C and 610 °C, hence being adapted all contexts of biochar quantification. The protocol 2, based on a narrower temperature interval, allowed more accurate values of biochar-Corg_{TR} quantification than protocol 1 due to lower overlapping between CO₂oxi emissions from soil and biochar. However, the protocol 2 can be used only when the biochar-C peak can be identified and well distinguished from soil-Corg_{TR}. Furthermore, the values of HI and OI, calculated based on hydrocarbons and CO₂pyr emissions from the pyrolysis stage of Rock-Eval®, may inform about the preferential source of Corg_{TR} between PyC and uncharred organic C. Indeed, low HI and OI values are consistent with high PyC content, as compared to unamended natural soils taken from the literature. Finally, the protocols presented in this study and using the Rock-Eval® method are fully adapted in experiments aiming to decipher the potential benefits of biochar on soil functioning and related ecosystem services. Further studies would be needed to better investigate the effects of weathering on soil and biochar thermal properties.

6. Author's contributions

Study conception and design was performed by David Sebag, Frédéric Delarue, Marie-Liesse Aubertin and Oscar Pascal Malou. Material collection was performed by Priscia Oliva, David Houben, Marie-Liesse Aubertin and Frédéric Delarue. Material preparation was performed by Marie-Liesse Aubertin and Oscar Pascal Malou. Analysis were performed by Marie-Liesse Aubertin. The first draft of the manuscript was written by Marie-Liesse Aubertin and all authors commented on previous versions of the manuscript. All authors read and approved the final manuscript.

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CRediT authorship contribution statement

Marie-Liesse Aubertin: Writing – original draft, Resources, Methodology, Data curation, Conceptualization. **Oscar Pascal Malou:** Writing – review & editing, Conceptualization. **Frédéric Delarue:** Writing – review & editing, Resources, Funding acquisition. **Priscia Oliva:** Writing – review & editing, Resources. **David Houben:** Writing – review & editing, Resources. **David Sebag:** Writing – review & editing, Resources.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Rock-Eval® is a trademark registered by the IFP Energies Nouvelles (IFPEN, France). The authors declare that they have no known competing financial interests or personal relationships that could appear to have influenced the work reported in this paper.

Data availability

All data supporting the findings of this study are available within the paper and its [Supplementary Information](#). Should any raw data files be needed in another format, they are available from the corresponding author upon reasonable request

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2024.116974>.

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