Quantifying soil organic carbon after biochar application: how to avoid (the risk of) counting CDR twice?

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Pyrogenic carbon capture and storage (PyCCS), which comprises the production of biomass, its pyrolysis, and the non-oxidative use of the biochar to create carbon sinks, has been identified as a promising negative emission technology with co-benefits by improving soil properties. Using biochar as a soil additive becomes increasingly common as farmers seek methods for soil improvement and climate change adaptation. Concurrently, there is growing interest in quantifying soil organic carbon (SOC) at the level of individual plots to remunerate farmers for their good agricultural practices and the resulting (temporary) carbon dioxide removal (CDR). However, methods currently applied in routine analysis quantify SOC, irrespective of its speciation or origin, and do not allow to distinguish biochar-C from SOC. As certification of PyCCS-derived CDR is already established using another quantification method (i.e., analysis of biochar-C content, tracking and registration of its application, and offsetting of carbon expenditures caused by the PyCCS process), the analysis of biochar-C as part of SOC may result in double counting of CDR. Hence, the objectives of this review are (1) to compare the physicochemical properties and the quantities of biochar and SOC fractions on a global and field/site-specific scale, (2) to evaluate the established methods of SOC and pyrogenic carbon (PyC) quantification with regard to their suitability in routine analysis, and (3) to assess whether double counting of SOC and biochar C-sinks can be avoided via analytical techniques. The methods that were found to have the potential to distinguish between non-pyrogenic and PyC in soil are either not fit for routine analysis or require calibration for different soil types, which is extremely laborious and yet to be established at a commercial scale. Moreover, the omnipresence of non-biochar PyC in soils (i.e., from forest fires or soot) that is indistinguishable from biochar-C is an additional challenge that can hardly be solved analytically. This review highlights the risks and limits of only result-based schemes for SOC certification relying on soil sampling and analysis. Carbon sink registers that unite the (spatial) data of biochar application and other forms of land-based CDR are suggested to track biochar applications and to effectively avoid double counting.

KEYWORDS

pyrogenic carbon capture and storage, carbon sink certification, carbon dioxide removal, pyrogenic carbonaceous material, black carbon, monitoring, reporting, verification

1 Introduction

Rising temperatures, water scarcity, prolonged droughts, and unexpected weather events are intensifying more than ever in recent history. These impacts are not surprising as the current atmospheric greenhouse gas (GHG) concentration is higher than at any point in the last 800,000 years. Altogether, global net anthropogenic GHG emissions were 59 ± 6.6 Gt CO_2eq in 2019, which was 12% higher than in 2010 (Canadell et al., 2021). To accelerate climate mitigation activities, a global framework was set to limit global warming to well below 2°C and pursue efforts to limit it to 1.5°C (United Nations, 2015). This goal can no longer be achieved by reducing emissions alone, and carbon dioxide removal (CDR) is necessary to transfer carbon (C) from the atmosphere into non-atmospheric C-sinks (Smith et al., 2020).

The European Commission recognizes the importance of industrial negative emission technologies, such as direct air capture with carbon storage (DACCS) and nature-based solutions for CDR. The buildup of soil organic matter (SOM) is a crucial element of nature-based solutions, which can be achieved through reduced tillage, reduced drainage, cover crops, and several other methods, including biochar (cf. definition in Table 1) application to soil (Whitman et al., 2010; Blanco-Canqui et al., 2020; COWI, EI, and IEEP, 2020; Don et al., 2024). In agriculture, biochar is used, among others, as a plant nutrient carrier, compost additive, animal bedding material, and soil conditioner to alleviate nutrient losses, stimulate buildup of soil organic carbon (SOC), counteract soil erosion, and improve soil water retention and long-term soil fertility under a changing climate (Blanco-Canqui et al., 2020; Schmidt et al., 2021). The production and non-oxidative application of biochar itself is considered a negative emission technology, often referred to as PyCCS (Schmidt et al., 2021; Lefebvre et al., 2023). In 2022, a still rather modest 100,000 t of CO_2 was removed from the atmosphere via PyCCS in Europe, but this number is expected to increase to up to 225 Mt. of CO_2 annually by 2036 (EBI, 2023). Globally, PyCCS may contribute to 6–35% of the negative emissions needed by 2,100 without generating undesirable side effects through land use change (Werner et al., 2021).

A certification of negative emissions is necessary for their financing, which requires the respective carbon removal technique to be quantifiable, deliver additional climate benefits, strive to store carbon for a long time, and contribute to effectively removing carbon from the atmosphere (COWI, EI, and IEEP, 2020). Accordingly, the EU suggested four QUantification, Additionality, Long-term storage, sustainabilITY (QU. A. L. ITY) criteria for industrial carbon removal certification methodologies (European Commission, 2022). Today, these carbon removals are certified by private companies according to their own guidelines or companies relying on independent third-party certification, e.g., the European Biochar Certificate (EBC)'s C-Sink Certificate (EBC, 2021). Either way, negative emission certificates are generated and sold on the voluntary market. A core element of a well-functioning market is that each negative emission can be certified only once. Avoiding double counting is essential to maintaining the integrity of the carbon removal systems and to collecting correct data for greenhouse gas inventories. Double counting of negative emissions may occur when more than one entity claims the same negative emission (Schneider et al., 2015; COWI, EI, and IEEP, 2020), e.g.,

TABLE 1 The definition of biochar and related materials.

Terminology	Definition
Biochar	"Biochar is a porous, carbonaceous material that is produced by pyrolysis of biomass and is applied in such a way that the contained carbon remains stored as a long-term C-sink or replaces fossil carbon in industrial manufacturing. It is not made to be burnt for energy generation" (EBC, 2012–2023).
Char	"The solid pyrogenic carbonaceous material remaining as a result of incomplete combustion processes such as those that occur in natural and man-made fire" (Bird et al., 2015).
Charcoal	Charcoal is a pyrogenic carbonaceous material that is deliberately produced by the pyrolysis of wood, seldomly of other biomass, that is used as a fuel, reductant, or chemical/material (Brown et al., 2015; Hagemann et al., 2018).
Pyrogenic carbon (PyC) or black C	"The thermochemically altered organic carbon fraction of pyrogenic carbonaceous material" (Bird et al., 2015).
Pyrogenic carbonaceous material (PCM)	PCM is an umbrella term for "all materials that were produced by thermochemical conversion and contain some organic C" (Lehmann and Joseph, 2015).
Soot	Soot are carbonaceous particles that are unintendedly formed by the recondensation of hydrocarbons in the gas phase during the incomplete combustion or pyrolysis of biogenic or fossil fuels (Lehmann and Joseph, 2015; Michelsen et al., 2020).

when biochar is certified as a biochar C-sink and as part of SOC increase, as detailed below.

For biochar, the certification process involves the quantification of its organic carbon (C_{org}) content and molar H-to-C_{org} ratio. Once soil application is confirmed, a fixed portion of biochar-C cannot be burned or oxidized by other means anymore (e.g., 74–93% when molar H to C_{org} ratio < 0.4) and the certification process is completed (Woolf et al., 2010; Budai et al., 2013; IPCC, 2019; EBC 2021–2023; Rodrigues et al., 2023). In contrast, result-based SOC certification schemes usually include repeated soil sampling and quantification of SOC to assess this (temporary) C-sink (Paul et al., 2023). However, as discussed in detail below, the quantification of SOC typically also includes biochar-C and other pyrogenic carbon (PyC) contained in pyrogenic carbonaceous materials (PCM, cf. Table 1) such as soot or wildfire-derived char. Therefore, e.g., the EBC C-Sink guidelines for certifying biochar C-sinks require that when farmers purchase certified biochar, they sign a contract that they are not participating in a SOC certification program to avoid double counting (EBC, 2021). This is a weak and hardly verifiable requirement that may be difficult to adhere to with the increasing interest in SOC certification and expanding the use of biochar. In addition, the prevailing inconsistencies in SOC monitoring protocols and the lack of standardized protocols in some regions could intensify the double-counting risk (Smith et al., 2020; Oldfield et al., 2022). Therefore, the extent to which non-pyrogenic SOC and non-biochar PyC can be quantified in routine soil analysis in the presence of biochar should be evaluated. Routine analysis here means that the method can be implemented with a high degree of automation and cost-effectively

on a large number of samples to enable a low-cost certification process. In Europe, costs for SOC determination can be as low as European €10 or less per sample according to the information provided by commercial laboratories and farmers. To date, many chemical, thermal, physical, spectroscopic, and molecular techniques have been developed for SOC and PyC differentiation and quantification (Hammes et al., 2007; Zimmermann and Mitra, 2017). Hence, this review aims to

i. Compare the physicochemical properties and the quantities of biochar and SOC fractions on a global and field/site-specific scale,
ii. Evaluate the established methods of SOC quantification, and
iii. Discuss existing analytical methods for PyC quantification and their suitability in routine analysis of biochar-C content in agricultural soils.

This review also aims to evaluate whether double counting of SOC and biochar C-sinks can be avoided via analytical techniques and to derive conclusions for reliable approaches for CDR certification when biochar is applied to soil.

2 Methods

Literature research was performed on Web of Science and Google Scholar covering the past 20 years. However, several articles published between 1990 and 1999 were also included due to their importance for the discussion. The following keywords were used during the article search: biochar; pyrogenic carbon continuum; soil organic carbon; soil organic carbon analysis; soil; biochar separation; biochar quantification in soil; pyrogenic carbon analysis; pyrogenic carbonaceous material; biochar carbon sink certification; carbon dioxide removal, CDR; double counting; carbon credits; pyrogenic carbon stocks; and fluxes. Care was taken to prioritize peer-reviewed publications and those articles that were written in English. However, several methods-related documents published in German were also included due to their importance in discussing analytical developments. Studies related to the PyC analysis in atmospheric samples were excluded. Priority was given to the recent PyC analysis involved with biochar-C analysis. After the initial screening, the articles were manually classified into different review sections.

3 Carbon speciation, stocks, and fluxes in soil and biochar

Biochar contains a wide range of organic and mineral components, whose mass fractions and speciation are determined by both the feedstock and the pyrolysis process parameters, such as temperature (Keiluweit et al., 2010; Singh et al., 2012; Bird et al., 2015; Rathnayake et al., 2020). Carbon speciation includes aliphatic and (polycyclic) aromatic hydrocarbons that form graphene-like sheets but may also comprise some residual non-pyrogenic compounds, e.g., from lignin; ash content can be in the range of 3–90% (Keiluweit et al., 2010; Hardie et al., 2014; Xiao and Chen, 2017; Ippolito et al., 2020).

SOC comprises a wide range of carbonaceous moieties, including carbon derived from readily decomposable plant debris and microbial biomass (i.e., cellulose, sugars, proteins, and lipids), lignin, waxes,

resins, tannins, and secondary metabolites from plants, humic substances, and PCM (Baldock and Skjemstad, 2000; Six et al., 2002; Lehmann and Kleber, 2015; Reisser et al., 2016). Pyrogenic carbonaceous material in soil exhibits overlapping physicochemical properties to that of biochar and is of both natural (e.g., wildfire char) and anthropogenic (soot) origins (Knicker, 2011; Santín et al., 2017). The continuum of PCM in soil, their formation pathways, initial reservoirs, and some basic physicochemical characteristics are indicated in Figure 1.

Both on a global level and the level of an individual plot of land, both non-pyrogenic and pyrogenic SOC are present and that might interfere during biochar-C analysis. Global PyC stocks due to PCM in soil range from 54 to 212 Gt (Supplementary Table S1). Depending on the fire intensity in the past, the PyC fraction in SOC varies globally, but also varies for land use type and soil texture, with agricultural land and clay soils rather showing higher PyC (Reisser et al., 2016). Apart from biochar, PCM enters soils via direct and indirect routes such as wild or manmade fires (land clearing, burning of crop residues, and unintended fires as a result of peatland drainage) and atmospheric depositions from incomplete combustion (soot), which is more prominent in upper soil horizons (Sanderman et al., 2021). Tillage, erosion, and surface runoff activities induce the horizontal and vertical movements of PCM in soils (Qi et al., 2017; Jiménez-González et al., 2021). The annual global input flux of PyC to the terrestrial environment via vegetation fires and fossil fuel burning ranges from 40 to 383 Mt. Yr^{-1} and 2 to 12 Mt. Yr^{-1}, respectively. The annual global biochar input flux is approximately 0.1 Mt. Yr^{-1} (Supplementary Table S1), and PyC loss due to remineralization ranges from 103 to 207 Mt. Yr^{-1} (Bird et al., 2015).

Depending on the soil types and PyC analytical methods used, the PyC content in soils could vary from 1 to 37% of SOC (Table 2). The application of 1–10 t ha^{-1} biochar to mineral soils with low-to-medium SOC content (it is uncommon to apply biochar to organic soils or minerals soil with high SOC) results in 2–18% of SOC being biochar-C nominally (Figure 2). According to that, the initial non-biochar PCM content in soil (4.3–5.6 t ha^{-1}) could be higher than a low biochar input (0.7 t ha^{-1} of biochar-C for 1 t biochar) to the soil.

4 Current methods to quantify SOC in routine analysis

4.1 Dry oxidation methods

The most widely used methods for determining SOC are based on dry oxidation. For this purpose, the sample is heated to a defined temperature, oxidized by pure oxygen, and the resulting CO_2 is quantified. Inorganic carbon, i.e., carbonates, must be removed by acid treatment prior to measurement and deducted to accurately calculate the C_{org} (VDLUFA, 1991; DIN EN 15936). Dry oxidation-based methods are simple, easy to automate, and have high throughput for smaller sample amounts (i.e., milligram levels). However, in principle, this method is similar to the method to measure biochar-C; e.g., the analytical guidelines of the EBC define the application of the DIN 51732, a dry oxidation procedure for solid fuels (Bachmann et al., 2016; Bird et al., 2017; EBC, 2012–2023). Given that the standard method for quantifying SOC and biochar-C analysis are practically the same, the SOC method will account for biochar as SOC.

Biomass	Slightly charred biomass	Biochar	Charcoal	Soot	Graphite
		Combustion residue		Combustion condensate	
		Pyrogenic carbonaceous material/ Black carbon			
Formation temperature (°C)	<300	350 - 750	200 - 600	>500	
Particle size	mm and large	cm to micron	cm to micron	micron to submicron	
O/C molar ratio	0.4 - 0.6	<0.4	0.2 - 0.4	<0.2	
H/C molar ratio	0.8 - 1.2	<0.7	0.4 - 0.8	<0.4	
Bulk density (g cm^{-3})	0.3 - 0.8	0.2 - 0.7	0.1 - 0.6	0.7 - 1.1	
Initial reservoir	Soil	Soil	Soil	Soil and atmosphere	

FIGURE 1

Continuum of pyrogenic carbonaceous materials (PCM) in soil (Hedges et al., 2000; Masiello, 2004; Wiedemeier, 2014; Bird et al., 2015; Santín et al., 2017; Wagner et al., 2018). This figure was created with BioRender.com.

4.2 Wet oxidation methods

Soil organic carbon can also be quantified by wet oxidation. Here, a mixture of potassium dichromate and sulfuric acid (sulfochromic oxidation) is added to the sample, followed by measuring the residual oxidizing agent (Agroscope, 2020) or the newly formed Cr (III) (ISO14235). While ISO14235 was withdrawn, sulfochromic oxidation is still used; e.g., it is the mandatory reference method in Switzerland (Agroscope, 2020) and the Soil Survey Standard Method in New South Wales, Australia (Department of Sustainable Natural Resources, New South Wales, 1990). The advantage of wet chemical approaches is that organic carbon (including amorphous organic carbon and PyC) is oxidized in a very targeted manner, whereas carbonates remain unaffected and are thus not detected. However, biochar or any other non-biochar PyC present in soil can be oxidized under the conditions applied in the Swiss reference method. Thus, biochar-C will be at least partially detected as SOC (Agroscope, 2020). In addition, Hardy and Dufey (2017) clearly showed that wet oxidation according to the Walkley–Black method will at least partially oxidize charcoal, with a potential impact of charcoal aging on its resistance to wet oxidation.

4.3 Analytical precision and minimal detectable difference (MDD)

For the Walkley and Black method of wet oxidation, the Global Soil Laboratory Network quantified a coefficient of variation (CV) of 2.7% when the sample contains 1% organic carbon (FAO, 2019). Assuming soils with low (31.7 t ha^{-1}) and medium (40.6 t ha^{-1}) SOC contents in the upper 20 cm [cf. Figure 2, soil data for Switzerland (Leifeld et al., 2005)], the addition of 0.7 t ha^{-1} biochar-C (e.g., 1 t of biochar with 70% C content) increases SOC by 2.2 and 1.7%, respectively. This change is lower than the CV and thus could not

be accurately measured. For the dry combustion method used in the elemental analyzer, Fliessbach et al. (2021) reported a 1–2% CV for a sample containing 0.73–2.6% of C; i.e., again, the addition of 1 t ha^{-1} biochar would not be recognized analytically.

However, the accuracy of SOC determination is not solely determined by analytical precision of organic carbon quantification but also, e.g., by spatial heterogeneity as well as the variability of soil bulk density that is needed to derive SOC stocks (t C ha^{-1}) from C_{org} (%C; Poeplau et al., 2017, 2020; Wiesmeier et al., 2020). Even under reasonably optimized conditions (100 samples per plot of 1–2 ha) to be applied for a sampling of scientific long-term experiments, Schrumpf et al. (2011) quantified an MDD of 1–2.5 t ha^{-1} of SOC for cropland and grassland sites, respectively. This further confirms that a single application of 1 t biochar (70% C_{org} content) would not be detectable, while larger applications (e.g., 3 t ha^{-1} biochar) and/or repeated application will quickly pass this level of MDD within the typical timeframes of 3–5 years (Wiesmeier et al., 2020) between repeated SOC quantification to detect stock changes. However, the MDD is likely to be higher for routine analysis when less than 100 samples are taken per plot for economic reasons.

5 Methods to quantify PyC contents in soils, their prospects, and limitations in the quantification of soil biochar-C content in routine analyses

Pyrogenic carbon in soil consists of a continuum of materials between the partly charred material and highly graphitized soot-like structures without clear-cut boundaries (Figure 1) (Schmidt et al., 2001; Knicker, 2011). The existing methods for quantifying, isolating, and characterizing PCM in soil attempt to differentiate the inorganic material, thermally unaltered organic carbon, and PyC using chemical,

TABLE 2 The percentage of PyC in total SOC in different soils as reported in previous studies using different analytical methods.

Soil type	Method used	PyC/SOC (%)	References
US agricultural soils	Hydrogen pyrolysis	2.7–7.7	Lavallee et al. (2019)
US agricultural soils	UV oxidation and ^{13}C NMR	10–35	Skjemstad et al. (2002)
Native grassland sites along a climosequence in North America	BPCA	4–18	Glaser and Amelung (2003)
Iberian top soils	MIR	3–20	Jiménez-González et al. (2021)
Southeastern Australian soils	MIR	7–37	Wang et al. (2018)
Australian agricultural and pastoral soils	CTO375	2–26	Qi et al. (2017)
Various soil types	CTO375, microscopy combined with ^{13}C NMR analysis, UV photooxidation combined with coulometry	4–6	Cornelissen et al. (2005)
Arable, permanent, and pasture grassland, forest, and urban soils collected from the Swiss Soil Monitoring Network	CTO375	1–6	Bucheli et al. (2004)
Peatlands	^{13}C NMR combined with molecular modeling	12.3–14.7	Leifeld et al. (2018)

NMR, nuclear magnetic resonance; BPCA, benzene polycarboxylic acid; MIR, mid-infrared spectroscopy; CTO375, chemothermal oxidation at 375°C. It is assumed that practically all of the listed PyC is from non-biochar origin as global biochar application is still extremely low.
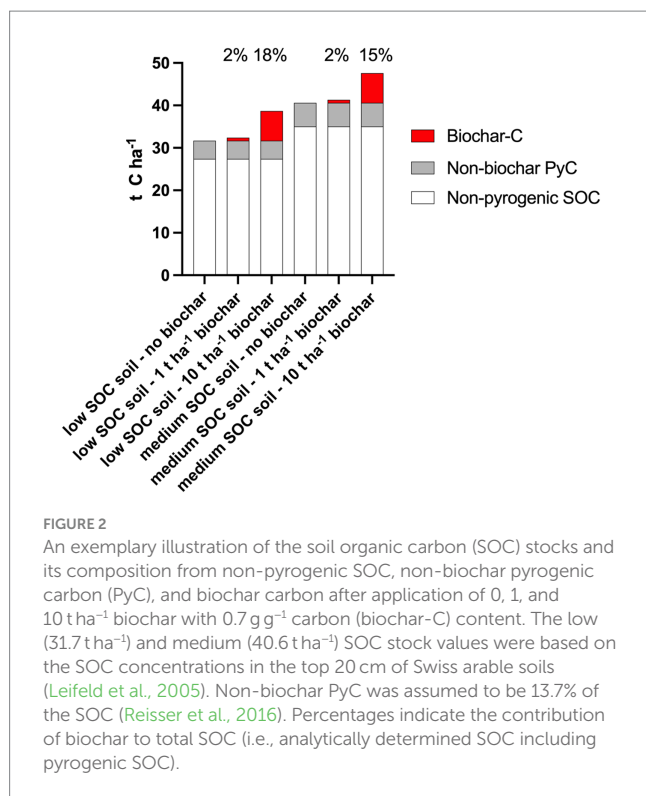
thermal, physical, spectroscopic, or molecular marker techniques (Bird, 2015). Due to technical limitations and variations in treatment severities, different methods isolate and characterize different fractions of the PyC continuum that are unique for the applied methodologies (Zimmermann and Mitra, 2017). Previous literature has thoroughly discussed these analytical methods in quantifying pyrogenic and non-pyrogenic fractions of SOC (Schmidt et al., 2001; Hammes et al., 2007; Wiedemeier et al., 2013; Bird, 2015; Hardy et al., 2022). Hence, this section and Table 3 only briefly summarize the prospects and limitations of currently available PyC analytical methods and evaluate their suitability for quantifying soil biochar-C in the presence of non-biochar PyC in soil with the goal of allowing quantification of non-biochar SOC in routine analysis.

Physical techniques used for the biochar separation from the soil are based on its visual appearance or differences in biochar material size or density compared to other non-biochar soil organic and mineral matter. When bigger biochar particles (> 2 mm) are applied to the soil, it is easier to physically separate by hand picking or sieving and by combining with microscopic techniques for further identification and verification (Spokas, 2013; Paetsch et al., 2017). However, due to the similar color (i.e., black) and depending on the abundance of non-biochar PCM in the soil, there can be biases to the overall quantified biochar content by hand picking or their visual appearance. Biochar in soil is subject to physical disintegration; i.e., particle size is reduced over time (Spokas et al., 2014; Sigmund et al., 2023), which will result in an underestimation of the soil biochar content. Alternately, biochar can be separated by flotation due to its bulk density, which is lower than soil mineral matter. Liquids with different densities, such as water (Sigmund et al., 2017) or sodium polytungstate solution (Singh et al., 2014), can be used. However, biochar in soil may form biochar mineral complexes whose density might be similar to that of bulk soil (Archanjo et al., 2017; Yang et al., 2021). Due to the overlapping bulk density, skeletal density, envelope density, and porosity values of biochar and other non-biochar PCM (Santín et al., 2017), the sensitivity and precision of density separation

methods can be lower. Physical methods can be extremely time-consuming and labor-intensive, and sample losses could occur during sample handling. Hence, physical techniques are irrelevant to biochar quantification in routine analysis. However, they may be useful in research to gain aged biochar for analysis or experiments.

The use of chemical techniques for quantifying biochar in soil depends on the oxidative resistance of the biochar carbon material compared to the other non-biochar SOC material. The methods include the use of NaClO, $K_2Cr_2O_7$, or UV-based oxidation methods. However, they could not effectively oxidize hydrophobic non-biochar SOC and may at least partially oxidize PyC (Hammes et al., 2007; Knicker et al., 2008; Meredith et al., 2013; Murano et al., 2021). Furthermore, the $K_2Cr_2O_7$ oxidation method exhibited good reproducibility and recovery for the chemical oxidation-resistant elemental carbon (COREC) content in plant char (i.e., plant material charred at 350°C under oxic conditions) mixed with HF-treated soil. Nevertheless, that method has not yet been validated for the biochar produced from various sources and soils with various amounts of non-biochar PCM.

Chemothermal oxidation method at 375°C (CTO$_{375}$) followed by elemental carbon analysis is a relatively simple, inexpensive technique to isolate and quantify PyC in soils (Gustafsson et al., 2001; Agarwal and Bucheli, 2011). However, pyrogenic artifacts could be formed if a sufficient amount of oxygen is lacking during the thermal treatment, lignin may partly survive the treatment, and some of the PyC can be oxidized entirely during the oxidation step, whereby the extent may vary for different soils as well as for PCM types (Agarwal and Bucheli, 2011; Gerke, 2019; Murano et al., 2021). Thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) offer the possibility to identify thermal signatures specific for SOC and biochar/other non-biochar PCMs. However, biochars show different signatures depending on the pyrolysis temperature, and also, soils may vary in their background signal (Leifeld, 2007; Hardy et al., 2022). Hence, unless the baseline soil (without biochar) exhibited distinct thermal signatures compared to that of biochar, it is harder to quantify biochar

FIGURE 2
An exemplary illustration of the soil organic carbon (SOC) stocks and its composition from non-pyrogenic SOC, non-biochar pyrogenic carbon (PyC), and biochar carbon after application of 0, 1, and 10 t ha^{-1} biochar with 0.7 g g^{-1} carbon (biochar-C) content. The low (31.7 t ha^{-1}) and medium (40.6 t ha^{-1}) SOC stock values were based on the SOC concentrations in the top 20 cm of Swiss arable soils (Leifeld et al., 2005). Non-biochar PyC was assumed to be 13.7% of the SOC (Reisser et al., 2016). Percentages indicate the contribution of biochar to total SOC (i.e., analytically determined SOC including pyrogenic SOC).

content in soil reliably. This method still needs to be validated for different biochars, different application rates, and soils with various amounts of native PCM and mineral compositions.

Hydropyrolysis (HyPy) is a thermal technique with high reproducibility that can be used to quantify the most stable fraction of PCM present in soil (Meredith et al., 2012). It measures the fraction of PyC that contains >7 aromatic ring structures with an H/C molar ratio of less than 0.5 (stable polycyclic aromatic carbon—SPAC) (Meredith et al., 2012). Wildfire chars exhibit considerably lower SPAC content (i.e., <30–40% on a dry ash-free basis) than biochar samples (i.e., SPAC content up to 75% on a dry ash-free weight basis [Santín et al., 2017]). Using HyPy may result in an underestimation of biochar's contribution to SOC as biochar also contains non-SPAC carbon, especially when produced at rather low temperatures, which might be certified as a temporary C-sink (Schmidt et al., 2022). Thus, HyPy still might not fully exclude double counting of CDR. In contrast, HyPy might overestimate the contribution of biochar-C to SOC for soil with high natural PCM content.

Koide et al. (2011) recently used an adapted loss on the ignition (heating sample at 550°C for 4 h) method to determine the soil biochar content. This method is simple and inexpensive, and no advanced analytical instruments are involved, only the muffle furnace and balance with the necessary precision. However, this method has to date only tested for extremely high biochar application rates (20–25 t ha^{-1}) and requires reference samples of both soil and biochar, which both hinders its application in routine analysis. Nakhli et al. (2019) significantly improved the loss-on-ignition method by looking at two different temperatures, but the need for the reference sample remains.

Benzene polycarboxylic acids (BPCA) is a molecular marker method used in soil PyC analysis (Schmidt et al., 2001). This method determines the condensed aromatic structure in PCM and does not produce pyrogenic artifacts during analysis. The conventional BPCA

method is time-consuming, prone to losing parts of the sample during filtering steps, and highly variable due to the different GC instrumental conditions and calibrations used (Hammes et al., 2007; Wiedemeier et al., 2016). Overestimation may arise from quantifying humic acid compounds such as PyC (Chang et al., 2018; Gerke, 2019).

The ^{13}C nuclear magnetic resonance (NMR) quantifies ^{13}C atoms in organic compounds and can identify the chemical bonds (Smernik, 2017). Both soil and biochar contain aliphatic-C and aryl-C. Hence, this method cannot differentiate biochar and non-biochar SOC, e.g., in humic acids. Methods based on IR are promising due to their simplicity, low cost, and potential to simultaneously determine multiple parameters beyond SOC, e.g., inorganic carbon and total nitrogen with one measurement (Baldock et al., 2013). However, their widespread application requires comprehensive reference databases that comprise spectra and calibrations for all types of soil that shall be investigated. In Australia, a national model for an MIR-based SOC determination was built based on 20,495 soil samples from 4,526 locations across the country (Baldock et al., 2013). Such comprehensive reference databases might even allow us to distinguish biochar and non-biochar PyC, as the site-specific reference spectra might also cover the different background concentrations of PyC. However, this needs to be proven separately. It also needs to be verified in detail to what extent the semi-persistent carbon fraction of biochar can also be detected by NIRS/MIRS as part of the biochar-C pool. In essence, IR-based methods are promising and have the potential to even reduce costs per sample, but require a tremendous investment to build the reference that would have to be accomplished by public actors, like the Commonwealth Scientific and Industrial Research Organization in Australia.

Isotopic carbon chemistry can also be used to delineate the biochar-C in the soil if their ^{13}C isotopic signatures are substantially different from the soils they applied (Bird et al., 2015). However, in reality, framers may apply biochar produced from various feedstock materials into the soil, originating potentially from both C3 and C4 plants with contrasting isotopic signatures, which hinders the application of isotope-based methods in routine analyses (Chalk and Smith, 2022).

Generally, all of these methods require considerable background knowledge about the site and biochar application history, partly high-tech equipment, or, in the case of near or mid-infrared (NIR/MIR) spectroscopy a site/soil-specific reference library, which is not yet routinely available. Thus, in the foreseeable future, it will hardly be possible to assess the MDD between biochar and other non-biochar PCM in biochar-applied soils with sufficient sensitivity, selectivity, and precision using currently available PyC analytical methods in routine analysis.

6 C-sink registry

An analytical solution to quantify non-biochar SOC is in itself only necessary as long as there is no confirmed or independently verifiable information as to whether, and if so at what dosage, biochar-C has been applied to a specific piece of land. Once such information is available, total SOC can be determined with state-of-the-art routine analysis (cf. Section 3), and the already-certified biochar-C could be simply subtracted arithmetically. Advanced biochar-based C-sink certification methods require the registration of

TABLE 3 Prospects and limitations of existing PyC analytical methods in distinguishing soil applied biochar-carbon from non-biochar PyC and from amorphous SOC.

PyC analytical method	Prospects	Limitations	Key references
Microscopic assessments, hand picking, or using solutions with different densities.	Simple and can be applied when sufficiently large PCMs are presented in soils.	Time-consuming and labor-intensive (thus, this can be expensive). Possible overlaps between different PCMs.	Singh et al. (2014) and Sigmund et al. (2017)
Chemical oxidation using NaClO or $K_2Cr_2O_7$ and UV photooxidation	Simple and well-established with detailed protocols and reference methods.	Inefficient removal of non-PyC substances present in SOC (i.e., lipids and waxy compounds) and limited selectivity between biochar and non-biochar PyC.	Simpson and Hatcher (2004), Hammes et al. (2007), Knicker et al. (2008), Meredith et al. (2013), and Murano et al. (2021)
CTO_{375} followed by elemental carbon analysis.	Simple and inexpensive methodology and easiness of controlling operating conditions.	Pyrogenic artifacts could be formed if a sufficient amount of oxygen is lacking during the thermal treatment. This method exhibits high selectivity toward soot-like PyC.	Gustafsson et al. (2001), Bucheli et al. (2004), Agarwal and Bucheli (2011), Gerke (2019), and Murano et al. (2021)
Thermogravimetry with differential scanning calorimetry (TG-DSC)	Simple and inexpensive methodology.	Difficult to reliably quantify amorphous and less stable PCM (i.e., charred wood and straw) present in soils due to overlapping signals. Hence, there is a limited selectivity between biochar and non-biochar PyC.	Leifeld (2007), Plante et al. (2009), and Hardy et al. (2022)
Adapted loss on the ignition method	Simple and inexpensive and no advanced analytical instruments are involved (only the muffle furnace and balance with necessary precision).	This method requires initial soil and biochar samples and biochar application history. When biochar promotes the formation of non-biochar SOC over time, the biochar content might be overestimated due to SOC increase.	Koide et al. (2011)
Hydropyrolysis (HyPy) followed by elemental carbon analysis	HyPy is a matrix-independent, high-precision, and highly reproducible technique for PyC quantification. It has been used to calibrate and validate the other PyC detection techniques.	Not yet widely used and established method. Possible overlap with soot.	Ascough et al. (2009), Meredith et al. (2012), and Cotrufo et al. (2016)
Benzene polycarboxylic acids (BPCA)	This method does not produce pyrogenic artifacts during analysis.	Time-consuming method, prone to losing parts of the sample during filtering steps. In addition, some PyC structures can be destroyed during the extraction resulting in underestimation of PyC.	Schmidt et al. (2001) and Cerqueira et al. (2015)
NMR spectroscopy	^{13}C NMR quantifies ^{13}C atoms in organic compounds, can identify the chemical bond, and is used to characterize biochars.	This method is time-consuming, expensive, and requires specific knowledge in instrumental handling and data evaluation and hence does not allow application in routine analysis.	Smernik (2017)
Near and mid-infrared spectroscopy	Rapid, economically viable, no chemicals involved, and non-destructive.	These methods need to be referenced against materials with known PyC content, calibrated, and validated with a wide range of PyC and soil types to be used in routine analysis with higher precision.	Jauss et al. (2017), Jiménez-González et al. (2021), and Pressler et al. (2022)
Isotopic methods	Economically viable, no chemicals involved, and non-destructive.	Considerable background knowledge about the site and biochar application history is necessary, which does not allow application in routine analysis.	Gustafsson et al. (2001), Bird et al. (2015), Ascough et al. (2016), Paetsch et al. (2017), and Pulcher et al. (2022)

biochar C-sinks in a public carbon sink registry containing all necessary information, such as biochar-C content and molar H to C_{org} ratio, the amount and date of applied biochar, and localization of the biochar C-sink (EBC, 2021; Etter et al., 2021; Puro.earth, 2024). However, farmers can apply biochar without C-sink certification and without entry into a carbon registry. In that case, no double accounting would occur when the total SOC of the soil is analyzed. However, if biochar C-sinks are valorized for CO_2-emission offsets on the voluntary market without registering the localized biochar application, the risk of double accounting is high. Therefore, biochar-based C-sinks may not be certified without listing on a public C-sink registry to make the above information available. When SOC-based C-sinks are certified, it is necessary to query the state or regional C-sink registry to verify how much C-sink-certified biochar was applied

during the SOC certification period in order to subtract the already-certified C-sink from the SOC C-sink certification.

Tracking systems are already established as a part of C-sink registers or in energy attribute certificates, which are issued to confirm the use of renewable energy (NREL, 2015). In addition, registers are used for certificates from emission avoidance and forestry; e.g., carbon credits created within the clean development mechanism had to be listed in the international transaction log provided by the United Nations Framework Convention on Climate Change (Lovell, 2010). Here, avoiding double use of certificates is the major goal, and spatial information is not included, which would be added information to C-sink registers. Currently, dedicated C-sink registers are offered, e.g., by C Capsule (Sheffield, United Kingdom), Puro.earth (Helsinki, Finland), and the Global Carbon Register Foundation (Arbaz, Switzerland). All providers mentioned above offer global applicability but differ in the details of the registered information. Each register may contain entries from all over the world. Thus, a single register query is currently insufficient to obtain the necessary information. This could be overcome either through geographical exclusivity of the registers or through a global (e.g., International Organization for Standardization (ISO)) standard for data structure and query procedures of such registers so that even information that may be distributed across different databases can be retrieved in a uniform manner. Geographical exclusivity could be achieved in the form of national registers run by federal offices or independent non-profit, non-governmental institutions (foundations) with a governmental mandate that would exclude the operation of any other non-connected register organization in the country. A description of the certification process for biochar and SOC C-sink using a carbon sink register to avoid double counting is explained in more detail in the Supplementary material with the aid of a hypothetical example (Supplementary Text 1).

7 Conclusion

Biochar production and biochar application to agricultural soils to build up SOC are two synergistic CDR methods. However, their combination is a challenge to the monitoring, reporting, and verification (MRV) of SOC buildup as there is a significant risk of double counting when biochar is applied, and SOC buildup is remunerated based on soil sampling and quantification of organic carbon. Based on this review, standard analytical methods for soil carbon are fit for purpose but cannot distinguish between SOC and PyC including biochar. More advanced methods can distinguish PyC from non-pyrogenic SOC but are complex, expensive, and not suitable for routine analysis. Moreover, none of these PyC analytical methods can sufficiently distinguish biochar-C from non-biochar PyC present in soil. Thus, there is a considerable risk of double counting of CDR when the production of biochar-C is certified and, at the same time, SOC certification based on result-based payments with sampling and organic carbon quantification performed on land to which biochar was applied. Hence, this risk can efficiently be addressed at the governance level using the following two steps: (1) all biochar-based carbon sinks shall be registered in a public C-sink register, and (2) when certifying SOC increase as CDR, the

public C-sink register shall be consulted to control that no certified biochar was applied to the respective field during the certification period. If biochar was applied, the SOC increase needs to be corrected arithmetically for the already-certified biochar-C. Similarly, SOC measurements taken for SOC-based CDR certification should be registered and geo-referenced to improve their MRV and to enable proper global carbon accounting considering the different types, permanence, and potential control periods of C-sinks. We, therefore, suggest the use of C-sink registers as a cost-effective tool to avoid double counting of CDR and improve overall carbon accounting for climate change mitigation. These registers should be implemented on regional, national, or supranational (e.g., EU) levels and should claim exclusivity for this respective area.

Author contributions

DR: Investigation, Writing – original draft. H-PS: Writing – review & editing. JL: Writing – review & editing. DB: Writing – review & editing. TB: Writing – review & editing. NH: Conceptualization, Funding acquisition, Writing – review & editing.

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Conflict of interest

H-PS and NH are members of the scientific advisory board of Carbon Standards International AG. H-PS is co-founder of the Global Carbon Register Foundation.

The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fclim.2024.1343516/full#supplementary-material

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Glossary

BPCA	Benzene polycarboxylic acids
CDR	Carbon dioxide removal
C_{org}	Organic carbon
CTO375	Chemothermal oxidation at 375°C
DACCS	Direct air carbon capture and storage
DIN	Deutsches Institut für Normung (German Institute for Standardization)
EBC	European Biochar Certificate
GHG	Greenhouse gas
HyPy	Hydropyrolysis
MDD	Minimum detectable difference
MIR	Mid-infrared spectroscopy
MRV	Monitoring, reporting, and verification
NIR	Near-infrared spectroscopy
NMR	Nuclear magnetic resonance
PCM	Pyrogenic carbonaceous material
PyC	Pyrogenic carbon
PyCCS	Pyrogenic carbon capture and storage
SOC	Soil organic carbon
SOM	Soil organic matter
TG-DSC	Thermogravimetry with differential scanning calorimetry