Science of the Total Environment 954 (2024) 176340

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Long-term biochar and soil organic carbon stability – Evidence from field experiments in Germany

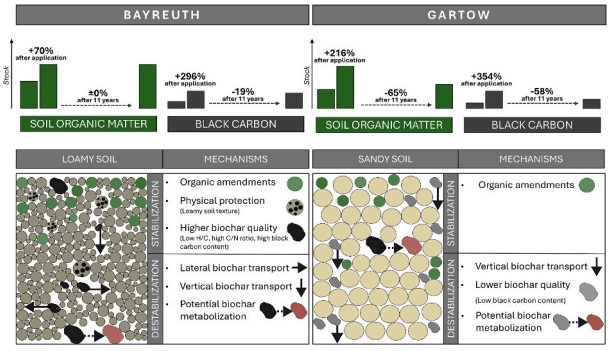
Arthur Gross *, Tobias Bromm, Steven Polifka, Daniel Fischer, Bruno Glaser

Soil Biogeochemistry, Martin Luther University Halle-Wittenberg, Halle (Saale), Germany

HIGHLIGHTS

- SOC sequestration after eleven years of biochar application on a loamy soil in northeastern Bavaria could be demonstrated
- Biochar application to a sandy soil led to large SOC dissipation, most likely due to lacking physical stabilization
- Aged biochar particles mainly lost labile black carbon compounds while stable compounds persisted

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Deyi Hou

Keywords:
Carbon sequestration
Biochar dissipation
Molecular marker
Carbon dioxide removal
Long-term biochar field experiment
Organic soil amendments

ABSTRACT

Organic soil amendments (OSA) with long residence times, such as biochar, have a high potential for soil organic carbon (SOC) sequestration. The highly aromatic structure of biochar reduces microbial decomposition and explains the slow turnover of biochar, indicating long persistence in soils and thus potential SOC sequestration. However, there is a lack of data on biochar-induced SOC sequestration in the long-term and under field conditions. We sampled two long-term field experiments in Germany, where biochar was applied 12 and 14 years ago. Both locations differ in soil characteristics and in the types and amounts of biochar and other OSA. Amendments containing compost and 31.5 Mg ha^{-1} of biochar on a loamy soil led to a SOC stock increase of 38 Mg ha^{-1} after OSA addition. The additional increase is due to non-biochar co-amendments such as compost or biogas digestate. After eleven years, this SOC stock increase was still stable. High biochar amount additions of 40 Mg ha^{-1} combined with biogas digestate, compost or synthetic fertilizer on a sandy soil led to an increase of SOC stocks of 61 Mg ha^{-1}; 38 Mg ha^{-1} dissipated in the following four years most likely due to lacking physical protection of the coarse soil material, and after nine years the biochar-amended soils showed only slightly higher SOC stocks (+7 Mg ha^{-1}) than the control. Black carbon stocks on the same soil increased in the short- and mid-term and decreased almost to the original stock levels after nine years. Our results indicate that in most cases the long-term effect on SOC and black carbon stocks is controlled by biochar quality and amount, while non-biochar co-amendments can be neglected. This study proves that SOC sequestration through the use of biochar is possible, especially in loamy soils, while non-biochar OSA cannot sequester SOC in the long term.

* Corresponding author.
E-mail address: arthur.gross@landw.uni-halle.de (A. Gross).

https://doi.org/10.1016/j.scitotenv.2024.176340
Received 7 June 2024; Received in revised form 30 August 2024; Accepted 15 September 2024
Available online 18 September 2024

1. Introduction

The growing world population (UN, 2015) and climate change are increasing pressures on soil resources and destabilize the world's food security (Tumwesigye et al., 2021). Sustainable agriculture must mitigate the consequences of current and future soil threats while adapting to future climate conditions and maintaining food production. Increasing pressure on soils already jeopardizes soil quality and several ecosystem functions, e.g., the role of soils as a C sink (FAO and ITPS, 2015). Soils are the most important terrestrial C sink, storing 3500–4800 Pg of C (Lehmann and Kleber, 2015), while terrestrial vegetation and the atmosphere store only around 800 Pg C each.

The centuries-long storage of organic carbon in the soil, better known as soil organic carbon (SOC) sequestration (Lal, 2008), is not only crucial for carbon dioxide removal (CDR) from the atmosphere, but also has a positive effect on soil health and promotes the functionality of ecosystems (Lal et al., 2007; Lal et al., 2015; Rumpel et al., 2020). Increasing the SOC storage can be achieved by using different organic soil amendments (OSA), the most common forms being straw, slurries, manures, compost, biogas digestates, sewage sludges biosolids. Often, these OSA are used for fertilization due to delivery of nutrients. However, since they contain varying amounts of C-rich organic compounds, the application of OSA leads to an increase of SOC stocks (Alvarenga et al., 2020). The aforementioned OSA types contain of very different forms of C-compounds, the majority of them possessing low stability and short mean residence times (MRT) in soil. Thus, these amendments need to be applied regularly, e.g. at the beginning of a new growing season to contribute to soil fertility and SOC stock increases in longer term (Alvarenga et al., 2020; Gross and Glaser, 2021). Biochar amendments, in contrast, contain highly aromatic C compounds and only little amounts of N (most of them being polycyclic and not available to microbes), and are, therefore, highly stable against microbial decomposition. When applied to soil, biochar's MRT is estimated to be 556 ± 483 years (Kuzyakov et al., 2014; Wang et al., 2016). However, adding pure biochar alone to soil does not necessarily improve the soil quality. Pure biochar added to soil can lead to immobilization of nitrogen and reduced plant growth (Kammann et al., 2015). Immobilization of N is more likely if the biochars C/N is very high (Mukome and Parikh, 2015) and the biochar was added without additional fertilizer as co-amendment or without a pre-treatment with nutrients, such as co-composting (Fischer and Glaser, 2012). Mixing biochar with compost has been shown to prevent N immobilization. Co-composting of biochar, moreover, leads to the formation of a coating on the surface of biochar that on the one hand serve as a slow releasing reservoir for nutrients and on the other hand protects the aromatic C structure of biochar from further oxidation while enhancing biochars stability in soil (Hagemann et al., 2017).

However, there is a lack of data on agricultural and environmental benefits of biochar in the long-term, specifically on a decadal time scale. In particular, biochar aging and the long-term fate of SOC stocks after biochar amendment remain poorly understood, as short-term studies and studies performed under laboratory conditions are not useful for predicting the long-term fate of biochar (Kuzyakov et al., 2014; Gross et al., 2021). Once applied to soil, biochar does not remain rigidly in place but reacts with the environment, with consequences for biochar's persistence, stability and traceability in soil. Biochar's persistence refers to the presence of biochar as opposed to its mineralization to CO_2 through biotic and abiotic processes (Lehmann et al., 2024), and thus persistence cannot be used as a synonym for stability. However, factors that influence the stability of biochar, can affect mineralization rates and thus persistence. This includes biotic processes such as the presence of microorganisms, but also larger soil fauna like earthworms. This includes chemical processes, mainly abiotic oxidation of biochar surfaces such as the reaction with water (Spokas and Reicosky, 2009) and desorption of CO_2 (Bruun et al., 2014). Last but not least, this includes the physical disintegration of large biochar particles into smaller particles (Spokas et al., 2014), due to frost, changing temperature and moisture, salt weathering, solubilization, roots or mechanical stress through e.g. soil tillage (Lehmann et al., 2024). Since biotic, chemical and physical processes typically occur simultaneously, and often sequentially while biochar resides in soil, experiments conducted under field conditions and with a feasible observation time are needed to achieve a more realistic idea about biochars soil persistence and stability. Many approaches exist to trace biochar in soil and to assess its stability. To distinguish biochar from other C compounds in soil, the aromaticity and degree of aromatic condensation of organic C compounds in soil can be used since they are a key feature of biochar. They can be measured using solid-state ^{13}C Nuclear magnetic resonance spectroscopy (NMR) or by using molecular markers, e.g. benzene polycarboxylic acids (BPCA) (De La Rosa et al., 2018; Glaser, 1999). The advantage of using molecular markers over e.g. quantification of labile and stable C pools in soils via thermochemical oxidation resistance methods is the unambiguity in distinguishing biochar quantity and quality/stability.

Short-term studies have shown ambiguous results on biochar stability (Knicker, 2011; Wang et al., 2016). This is due to the fact that mainly the labile biochar-C is decomposed in the short-term (Wang et al., 2016). These labile fractions decompose rapidly, leading to a positive priming effect. However, it has been observed that in the long-term, pyrogenic organic matter may promote physical protection through sorption, leading to negative priming at a later stage (Maestrini et al., 2015). So far, only a few studies have observed comparable negative priming effects in field experiments following the application of biochar (Blanco-Canqui et al., 2020; Guo et al., 2024). Thus, studies that solely focus on short-term effects underestimate biochar's true MRT considerably. A recent meta-analysis on the potential of biochar to increase the soil C stock in agricultural soils indicates the high persistence of biochar contributing to an additional build-up of SOC with increasing observation time (Gross et al., 2021). The organic C stocks increased significantly over a period of up to ten years. However, this observation was very limited in the number of included studies, and studies with a duration longer than ten years were missing completely.

This research gap is unfortunate, because efficient CDR technologies are urgently needed, and the European Union (EU) is pursuing CO_2 neutrality by 2050 as part of the “Green-Deal”. To achieve this ambitious goal, the EU Commission proposed a net reduction in emission of greenhouse gases of 55 % by 2030 compared to 1990 emission levels as a milestone for the new EU climate law.

The aim of this study is to provide insights into long-term SOC and biochar stock dynamics on a decadal scale and under field experiment conditions. The first objective was to analyze the SOC stock dynamics over time after the application of varying biochar amounts at two different long-term biochar field experiments in Germany. In addition to SOC, as a second objective, we analyzed the black carbon stocks, which we used as a molecular marker for biochar, to verify whether the biochar applied long ago is still traceable and stable, and to quantify its remaining amount. The third objective was to analyze the influence on the SOC stocks induced by different organic and mineral fertilizers used as co-amendment to biochar application and to determine whether they still had a co-effect on SOC sequestration and biochar stability at the two different sites, eleven and nine years after application.

2. Material and methods

2.1. Study area and experiment characteristics

To achieve the objectives of this study, two long-term field experiments located in Germany were examined (Fig. 1).

Both field experiments used biochar-treated fertilizers and cover different soil conditions. Table 1 summarizes the main characteristics and properties of the two experimental sites.

One of the two field experiments is located near Bayreuth (Donndorf) in northeastern Bavaria and was established in 2010 to analyze the

effects of different organic soil amendments (OSA), consisting of biochar mixed with compost in different amounts, on soil properties and crop yields under organic farming conditions (Fig. 1). The experimental site covered a total area of 3600 m^2 (30 m × 120 m) and consists of 50 individual plots of 72 m^2 (6 m × 12 m), each of them arranged according to a Latin rectangle in a row-column design so that each of the ten treatments was present in each row and each pair of columns in a grid across the field (Fig. S1a; Meyer et al., 2012). Each of the ten treatments was replicated five times and each experiment plot received a OSA treatment in July 2010. The organic material was applied and distributed on the plots manually. Afterwards, it was incorporated to a depth of 10 cm using a rotary tiller. Biochar containing treatments were applied once, while compost was applied every experiment year until 2012. Total C input by each of the treatment is shown in Fig. S2. From 2012 on, all plots have been treated equally with organic fertilizers every year since then, either with maize biogas digestate using a liquid manure spreader or by broadcasting cow or horse slurry at amounts of about 15–30 Mg ha^{-1}. More details on the Bayreuth field experiment can be found in Meyer et al. (2012) and Cooper et al. (2020).

The second experimental site is located in the Wendland region, near Gartow in northern Germany (Fig. 1). The experiment was established in 2012 with the objective to compare different OSA from regional agricultural residues, including biochar, with synthetic fertilization in their effects on soil properties, nutrient dynamics, and crop yields. Similar to the Bayreuth site, the experiment field consisted of 50 individual plots of 72 m^2 (6 m × 12 m), arranged as a Latin rectangle (Fig. S1b; Glaser et al., 2015). Due to the space between plots which were used as driving lanes, the total area was 7200 m^2 (60 m × 120 m). Ten different treatments were tested in five-fold replication (Fig. S1b). Total C input by each of the treatment is shown in Fig. S2. All biochar treatments except the ones containing of 1 Mg ha^{-1} were applied once at the beginning of the experiment in May 2012. All other treatments received annual applications for three years in spring (including 3 times 1 Mg biochar per hectare summing up to 3 Mg biochar per hectare in total after application). The organic material was applied and distributed on the plots by hand, and incorporated into the first 15 cm using a disc harrow. The experiment discontinued in fall 2014 after the last harvest and all plots have been treated with biogas digestate every year in spring since then. In 2020 and 2021, the plots were amended with compost in spring. More details on the Gartow field experiment can be found in Glaser et al. (2015).

Table 1
Main site characteristics, soil properties and biochar properties of the two biochar field experiments in Bayreuth and Gartow.

	Bayreuth (Northeastern Bavaria)	Gartow (Eastern Lower Saxony)
Site characteristics		
Latitude	49°56′01.7″	53°01′09.26″
Longitude	11°31′17.1″	11°29′50.04″
Precipitation [mm]	507	575
Temperature [°C]	8.2	8.8
Current use	Cropland	Cropland
Tillage depth [cm]	0–10	0–20
Soil properties [0–30 cm]		
Soil type	Cambisol	Cambisol
Soil texture	Sandy loam	Sand
Sand [%]	62	94
Silt [%]	12	4
Clay [%]	26	2
Initial SOC [%]	1.6	0.6
pH	5.4	5.7
Biochar properties		
Feedstock	Pine wood	Green cuts
Pyrolysis temperature [°C]	550	650
Total carbon [g kg^{-1}]	843	667
Total nitrogen [g kg^{-1}]	4	30
Black carbon [g kg^{-1}C]	795	259
C/N	239	75
H/C [atomic ratio]	0.11	0.1–0.2
pH [H_2O]	9.8	10.3
Ash [g kg^{-1}]	90	230

2.2. Soil sampling and preparation

At the Bayreuth site, soil sampling was conducted twice in 2010 (immediately prior to and one month after the soil was amended in July). In 2011, 2013, 2016 and 2021 soil samplings were conducted after harvesting in fall. Between 2009 and 2016, samples were taken at two depths (0–10 cm and 10–30 cm), and in 2021 in 0–30 cm. At the center of each plot, three to five samples were taken using an auger and were then mixed into one composite sample.

At Gartow, soil sampling was conducted in 2012 (immediately before and after amendment application in May), twice in 2013 (May and September), twice in 2014 (May and September), once in 2016 and 2021. From 2012 to 2016, sampling was conducted at two soil depths (0–10 cm and 10–30 cm), whereas in 2021, samples were gathered from a unified depth of 0–30 cm. At the center of each plot, two to five samples were taken using an auger and then mixed into one composite sample.

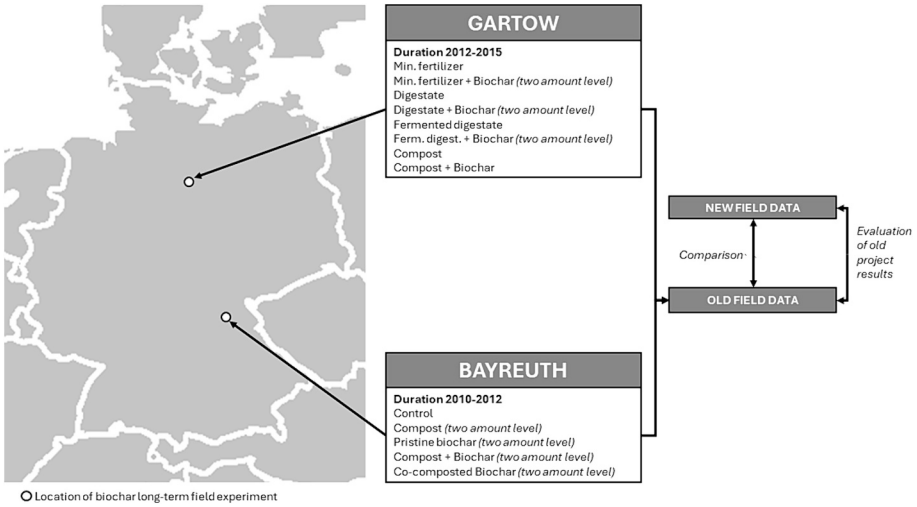


Fig. 1. Location of the investigated biochar field experiments and the scope of this study.

The soil samples from both locations were dried in an oven at 40 °C for a duration of 48 h. In preparation for further analysis, the samples were ground using a vibratory disc mill.

2.3. Soil analysis

2.3.1. Soil organic carbon and black carbon

SOC was determined by dry combustion using a CN elemental analyzer (Elementar Vario El, Heraeus, Hanau, Germany). Every sample was treated with diluted hydrochloric acid to eliminate inorganic C. Samples were measured as complete time series of each treatment to avoid a systematic offset over time.

To analyze black carbon contents, we used the benzene polycarboxylic acids (BPCA) method of Glaser et al. (1998), modified by Brodowski et al. (2005). Individual BPCA were isolated and measured using a Shimadzu GC 2010 gas chromatograph, equipped with a flame ionization detector and an HP5 column (30 m × 0.25 mm × 0.25 μm). The total black carbon content was determined by calculating the sum of BPCA, which was then converted into biochar equivalents using the factor 2.27 (Glaser et al., 1998). To assess the aromaticity of the samples, the relative contribution of the sum of hemimellitic, trimellitic and trimesic acid (B3CA), the sum of pyromellitic, melophanic and prehnitic acid (B4CA), benzene pentacarboxylic acid (B5CA) and mellitic acid (B6CA) was used.

2.3.2. Soil texture, bulk density, and carbon stocks

Soil texture was estimated based on the particle size distribution that was analyzed using laser diffractometry. Contents of silt, clay and SOC were then used to estimate bulk density (BD) using the pedotransfer function given in Men et al. (2008) (Eq. (1)).

$$Bulk\ density = 1.386 - 0.078 \times SOC + 0.001 \times Silt + 0.001 \times Clay \quad (1)$$

where BD is expressed in g cm^{-3} and the SOC, silt, and clay content in %.

The use of a pedotransfer function to estimate BD was necessary since BD was not measured in the field consecutively at each sampling date. The estimated BD, however, was compared with that measured in the field, when available, to verify its plausibility.

In this study, SOC and black carbon are expressed as stocks. Carbon stocks were quantified using an equation, provided by FAO (2019) (Eq. (2)).

$$Carbon\ stock = Carbon\ content \times Bulk\ density \times Depth \times 0.1 \quad (2)$$

where the carbon stock (SOC or black carbon) is expressed in Mg ha^{-1}, bulk density in g cm^{-3}, layer thickness in cm and the carbon content (SOC or black carbon) in g kg^{-1}.

The calculation of SOC and black carbon stocks was essential for comparing data obtained from soil depths of 0–10 cm and 10–30 cm prior to 2021 with data from 2021, which was collected from a unified soil depth of 0–30 cm. In addition, with this approach it was possible to calculate the recovery of applied biochar and other OSA.

2.4. Statistical analysis

Statistical analysis was carried out using R 4.1.2 (R Core Team, 2021). The differences of SOC and black carbon stocks among different sampling dates in time were analyzed using a linear mixed-effects model (random-intercept model), as the observed variable (SOC or black carbon) eventually becomes dependent through repeated measuring the same plots. In such cases, mixed-effects models should be used since we assume fixed effects (e.g., treatments and application amounts) and multiple random effects (rows, columns, and time) to influence our model results (Piepho et al., 2003). Separate mixed-effects models were carried out to analyze temporal differences between the different sampling dates in time within a certain amount level (low and high added biochar amounts). All individual treatments per field experiment were therefore aggregated according to the amount of biochar added (Fig. S2). In our mixed-effects model, we focused on the amount levels because according to analysis of variance (ANOVA), the individual biochar treatment structure (except for one single treatment in Gartow, see Table S2) showed no significant effects on SOC and black carbon stocks in Bayreuth and Gartow in 2021, respectively. What did, however, matter was the biochar amount added. Details on the conducted ANOVA and the obtained results can be found in the Supplementary Material file.

Only the time series containing biochar additions were statistically evaluated since our focus was the long-term effect of biochar, but non-biochar treatments are included in the box-plots of the results section for a visual impression of their effects on the C stocks. Each of the four time series started with the first sampling date after the addition of biochar, thus the initial SOC and black carbon stock was excluded, since we wanted to analyze the differences after the application of biochar. Additionally, the SOC and black carbon stock time series in 0–10 cm and 10–30 cm soil depth between 2010 and 2013 in Bayreuth and 2012–2016 in Gartow was analyzed, to investigate vertical biochar transport with time. Only the variants with a high biochar content were used for the evaluation, as they showed pronounced effects. In addition, the black carbon data of the high biochar variants from the 2016 sampling in Gartow showed many data gaps, while the variants with a high biochar content were complete. Therefore, the 2016 black carbon data from Gartow was only used to evaluate vertical transport. Mixed-effects modelling was conducted using the R package lme4 (Bates et al., 2015). Variance components were estimated with the residual maximum likelihood (REML) method (Kenward and Roger, 1997). In order to meet parametric model conditions, a Box-Cox transformation was performed in the case of non-normal model residuals. Significant effects were observed along the time series of each biochar amount level at each of the two field experiments using the estimation of least-squares means with the R package emmeans (Lenth et al., 2023). Results of this post-hoc test are provided in Tables S4 and S5 of the Supplementary Material file. Significant effects are marked with one, two or three asterisks in the results tables, depending on the level of significance ($p < 0.05$*; $p < 0.01$**; $p < 0.001$***).

3. Results

3.1. Effects of different biochar amounts on temporal soil organic carbon dynamics

The addition of OSA containing low biochar amounts (9 Mg ha^{-1}; total C inputs are shown in Fig. S2) led to an initial median SOC stock increase of 17 Mg ha^{-1} at the Bayreuth site (Fig. 2; from 54 to 71 Mg ha^{-1}, +31 %). In the following three years, the median SOC stock slightly decreased (−9 Mg ha^{-1}, −13 %) and increased again between 2013 and 2021 (from 63 to 76 Mg ha^{-1}, +21 %), but both changes were not significant (Table 2). A comparable temporal dynamic was observed when high biochar levels (31.5 Mg ha^{-1}) were added. Initially, the median SOC stock increased by 38 Mg ha^{-1} (from 54 to 92 Mg ha^{-1}, +70 %) and remained at the same level until 2021 (Fig. 2). At the Gartow site, OSA additions containing 3 Mg ha^{-1} of biochar initially led to an SOC stock increase of 8 Mg ha^{-1} (from 21 to 29 Mg ha^{-1}, +38 %). The SOC stock significantly decreased by 17 % between 2012 and 2014 to 24 Mg ha^{-1} (Fig. 2, Table 2, and Table S4). Between 2014 and 2016, the SOC stock remained at almost the same level and increased slightly but not significantly between 2016 and 2021 (from 24 to 28 Mg ha^{-1}, +17 %). The addition of OSA mixed with 40 Mg ha^{-1} of biochar led to an overall SOC stock increase of 61 Mg ha^{-1} (from 22 to 83 Mg ha^{-1}, +277 %). One year later, in 2013, the SOC stock dropped by 31 Mg ha^{-1} and continued to significantly decrease by 37 % between 2013 and 2014 to 41 Mg ha^{-1} (Fig. 2). Between 2014 and 2016, the median SOC stock slightly increased to 46 Mg ha^{-1} (+12 %), but this change was not significant. In the following five years, the median SOC stock dropped

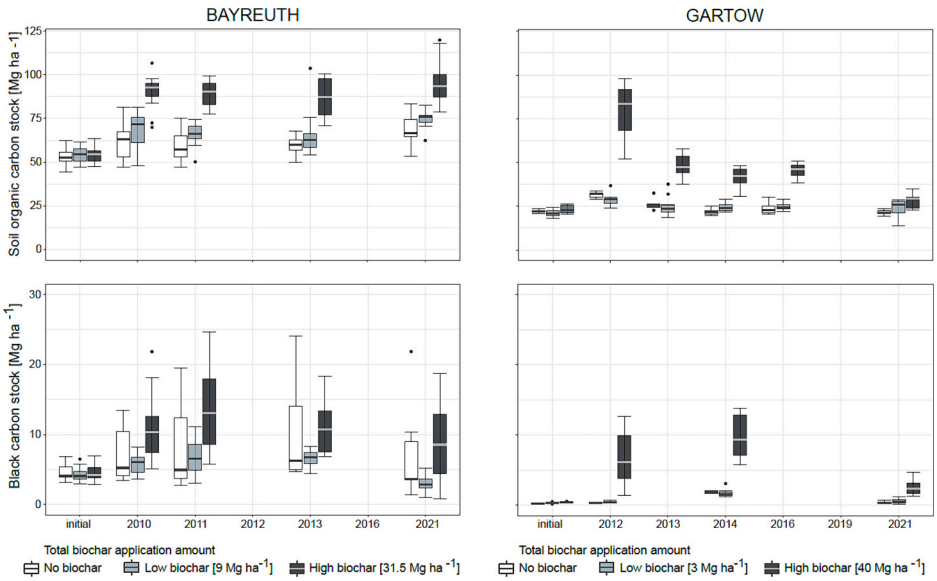


Fig. 2. Box plots of soil organic carbon stock and black carbon stock time series in the Bayreuth and Gartow field experiment (soil organic carbon stock data from fall 2013 and 2014 in Gartow are not shown). The median of the data is shown as a horizontal solid line within the box. Each box contains the middle 50 % of the data of a category. The whiskers indicate the lower and upper quartile of the data, respectively, and are limited to 1.5 times the interquartile range. Black dots outside the whiskers represent outliers.

Table 2
Results of linear mixed-effects model analysis of the soil organic carbon stocks time series at both locations. Separate mixed-effects models were carried out for each amount (low and high) to analyze the effect of the different sampling dates in time (year). numDf = degrees of freedom in the numerator; denDf = degrees of freedom in the denominator.

	numDf	denDf	F value	*p* value
Bayreuth				
Low biochar (9 Mg ha^{-1})				
Row	4	6	3.59	0.08
Column	4	6	9.79	<0.01**
Year	3	42	0.35	0.79
High biochar (31.5 Mg ha^{-1})				
Row	4	6	4.20	0.06
Column	4	6	2.09	0.20
Year	3	42	1.62	0.20
Gartow				
Low biochar (3 Mg ha^{-1})				
Row	4	5	0.91	0.52
Column	4	50	0.41	0.80
Year	6	50	3.43	<0.05*
High biochar (40 Mg ha^{-1}) - Box-Cox transformed				
Row	4	6	1.45	0.33
Column	4	6	1.29	0.37
Year	6	84	37.99	<0.001***

significantly by another 17 Mg ha^{-1} (−63 %).

3.2. Effects of different biochar amounts on temporal black carbon dynamics

At the Bayreuth field experiment, the addition of OSA containing low biochar amounts increased the black carbon stocks initially by 200 % (2 Mg ha^{-1} to 6 Mg ha^{-1}) (Fig. 2). In the following three years, the black carbon stock remained stable (Table S5). Initially, the addition of 31.5 Mg ha^{-1} of biochar combined with co-amendments significantly increased the black carbon stock by 50 % (8 Mg ha^{-1} to 12 Mg ha^{-1}), increased the stock again by 3 Mg ha^{-1} in the following year (+25 %), and led to a significant drop back to 12 Mg ha^{-1} (−20 %) in 2013 (Table 3 and Table S5). Between 2013 and 2021, the black carbon stock remained stable. The addition of 3 Mg ha^{-1} mixed with co-amendments on the sandy soil in Gartow did not change black carbon stocks significantly (Fig. 2). The addition of OSA containing 40 Mg ha^{-1} of biochar increased the black carbon stock by 28 % (7 Mg ha^{-1} to 9 Mg ha^{-1}) and did not change significantly over the next two years. In the long-term, however, the median black carbon stock dropped by 56 % (5 Mg ha^{-1} to 4 Mg ha^{-1}) and was therefore just slightly higher than initially before the application (2 Mg ha^{-1}).

Table 3
Results of linear mixed-effects model analysis of the black carbon stocks time series at both locations. Separate mixed-effects models were carried out for each amount (low and high) to analyze the effect of the different sampling dates in time (year). numDf = degrees of freedom in the numerator; denDf = degrees of freedom in the denominator.

	numDf	denDf	F value	p value
Bayreuth				
Low biochar (9 Mg ha^{-1})				
(Intercept)	1	42.00	4175.17	<0.001***
Row	4	6.00	0.41	0.80
Column	4	6.00	7.25	<0.05*
Year	3	42.00	77.94	<0.001***
High biochar (31.5 Mg ha^{-1}) - Box-Cox transformed				
(Intercept)	1	42.00	7405.61	<0.001***
Row	4	6.00	3.69	0.08
Column	4	6.00	1.14	0.45
Year	3	42.00	5.37	<0.001***
Gartow				
Low biochar (3 Mg ha^{-1})				
(Intercept)	1	23.00	1057.14	<0.001***
Row	4	5.00	0.71	0.62
Column	4	23.00	0.26	0.90
Year	3	23.00	11.45	<0.001***
High biochar (40 Mg ha^{-1})				
(Intercept)	1	42.00	235.22	<0.001***
Row	4	6.00	2.23	0.18
Column	4	6.00	0.46	0.76
Year	3	42.00	7.75	<0.001***

3.3. Effects of biochar additions on temporal soil organic carbon and black carbon dynamics in different soil depth

After the addition of OSA containing high biochar amounts (31.5 Mg ha^{-1} in Bayreuth and 40 Mg ha^{-1} in Gartow), SOC and BC stocks in 0–10 cm significantly decreased with time. In Bayreuth, the SOC stock of 52.8 Mg ha^{-1} in 2010 after the addition of biochar decreased by 42 % to 30.45 Mg ha^{-1} in 2013. Black carbon stocks decreased by 67 % from 8.54 to 2.79 Mg ha^{-1} in the same time period. In Gartow, the SOC stocks in 0–10 cm decreased from 34.27 to 17.08 Mg ha^{-1}, corresponding with 50 % between 2012 and 2016. Black carbon stocks decreased by 68 % from 7.27 to 2.33 Mg ha^{-1}. In 10–30 cm soil depth, SOC and black carbon stocks significantly increased with time at both locations. In Bayreuth, SOC stocks increased by 30 % from 39.63 to 51.58 Mg ha^{-1}, while black carbon stocks increased by 135 % from 3.25 to 7.36 Mg ha^{-1}. In Gartow, SOC stocks in 10–30 cm increased by 58 % between 2012 and 2016 while black carbon stocks increased by 1010 % from 0.28 to 3.11 Mg ha^{-1}.

3.4. Long-term effects of different biochar treatments on biochar quality

Biochar of the Bayreuth field experiment contained three time as much black carbon compared to the biochar used for the Gartow field experiment (Table 1), indicating a higher biochar stability of the former. In addition, the relative contribution of higher aromatic BPCA (B5CA and B6CA) increased between 2010 and 2021 in all high biochar treatments at Bayreuth (Fig. 3). Apart from the biochar (40) digestate, the relative contribution of higher aromatic BPCA slightly decreased over time between 2012 and 2021 in all treatments containing high biochar amounts of the Gartow field experiment (Fig. 3).

4. Discussion

4.1. Long-term effects of biochar treatments on SOC stock changes

It is known that the addition of biochar increases SOC stocks (Gross et al., 2021; Huang et al., 2023), however, little is known about the long-term effects under real agronomic field conditions. In a recently published meta-analysis, the longest observation duration under field experiment conditions was ten years (Gross et al., 2021). According to this study, SOC stocks of biochar-amended soils were significantly higher than the control soil after nine and eleven years, but only if high amounts of 31.5 Mg ha^{-1} of biochar at the Bayreuth site and 40 Mg ha^{-1} of biochar at the Gartow site were added (Table S1). However, both sites investigated showed contrasting SOC stock dynamics over time (Fig. 2). At the Bayreuth site, the initial SOC stock increases induced by high amounts of biochar addition could be stabilized over time (Fig. 2). Black carbon stocks slightly decreased within the same time period, indicating that the additional SOC must not have originated from the biochar itself. This finding corroborates with results of Blanco-Canqui et al. (2020), who made similar observations on a loamy soil under reduced tillage in southwestern Iowa. Negative priming has previously been found to be positively correlated with soil clay content and the pyrolysis temperature of the biochar (Ding et al., 2018). Maestrini et al. (2015) found that with increasing time, biochar could further enhance SOC accumulation through adsorption and physical protection of dissolved organic C. Whether the SOC buildup observed in our study was due to negative priming effects, the initial high compost application (70 Mg ha^{-1}) or the co-composting of the biochar, or due to the organic farming practices including reduced tillage and annual manure input after discontinuation of the experimental treatment, could not be determined certainly, since the SOC stocks of the high biochar- containing OSA showed a large dispersion (Table S3). What could be concluded however, was that the initial SOC build-up by the biochar reached a new and high plateau, which has been stabilized over a period of eleven years. In contrast, the Gartow experiment showed pronounced SOC dissipation over time at both amounts of added biochar (3 and 40 Mg ha^{-1}). Polifka et al. (2018) showed that the more biochar was added, the more CO_2 was released, up to 60 %. However, most of this CO_2 was C4-derived and therefore, not due to biochar or SOC. More likely, the elevated CO_2 stems from mineralization of the maize-based biogas digestates and C4 plant residues, since maize was cultivated in the years before the gas

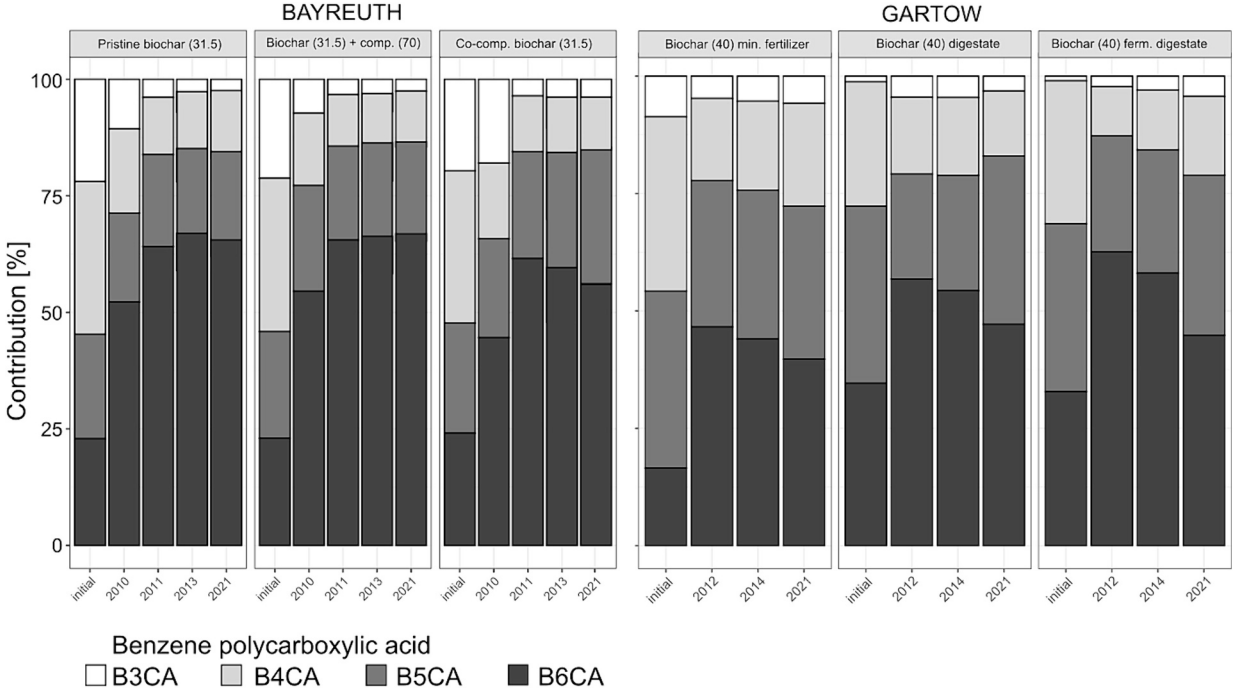


Fig. 3. Relative contribution of the sum of hemimellitic, trimellitic and trimesic acid (B3CA), the sum of pyromellitic, melophanic and prehnitic acid (B4CA), benzene pentacarboxylic acid (B5CA) and mellitic acid (B6CA) to the sum of all BPCA of each of the treatments containing high biochar amounts of both field experiments.

measurement. Due to the same C3-isotope composition of soil organic matter and the applied biochar, it is not possible to differentiate between biochar-derived and soil organic matter-derived emitted CO_2. However, compared to the high amount of biochar added (40 Mg ha^{-1}), additional CO_2 release from biochar and SOC was negligible (about 0.1 Mg ha^{-1}). There is still no consensus about how the added biochar affects the priming of native SOC due to the very complex interplay between various biochar treatments, soil properties and the soil microbial community (Rasul et al., 2022). These contrasting SOC stock dynamics observed in our data might, therefore, be related to the different soil properties, and the different biochar properties of the two field experiments, especially the higher polycondensed aromatic carbon content of the biochar used at the Bayreuth experiment.

4.1.1. Influence of location properties on SOC stock changes

Most obviously, both locations show a different soil texture. While the soil at the Bayreuth site contains 12 % silt and 26 % clay, the soil texture at the Gartow site is dominated by 95 % sand. Texture is one of the most important influencing factors of amendment-induced SOC stabilization (Han et al., 2016; Berhane et al., 2020; Gross and Glaser, 2021; Gross et al., 2021). Soils with a finer texture have higher amounts of clay minerals and iron oxides. These components not only protect SOC from enzymatic breakdown and turnover as noted by Nannipieri et al. (2018) and Zhang et al. (2019), but also increase SOC stability in the form of physical protection within soil aggregates, according to Lal (2018) and Zong et al. (2018). Conversely, sandy soils offer less of this physical protection, making SOC more susceptible to oxidation and decomposition (Gross et al., 2021), which leads to positive SOC priming (Rasul et al., 2022), along with losses of SOC through leaching and runoff (Yang et al., 2019). On average, the increases in SOC stock post-biochar application were higher in silty (13 Mg ha^{-1} and 31 %), loamy (15 Mg ha^{-1} and 25 %), and clayey soils (18 Mg ha^{-1} and 52 %) compared to sandy soils (6 Mg ha^{-1} and 21 %) (Gross et al., 2021).

In principle, our results support the findings of the mid-term SOC effects that were found at the Bayreuth site (Cooper et al., 2020) and the Gartow site (Greenberg et al., 2019). The latter study found that the co-amendment of fertilizers had no effect on SOC after four years, which we now can confirm after a duration of nine years (Table S1). Greenberg et al. (2019) additionally analyzed SOC in different aggregate size fractions and found slight SOC increases after the application of 40 Mg ha^{-1} of biochar in the 0.25–0.053 mm and $<$ 0.053 mm fractions, the most stable aggregate size fractions. Since they did not differentiate between unpyrolized and pyrolized organic C, they argued that increased content of SOC in the fine fractions might be related to higher crop yields and thus higher plant-derived inputs to SOC. Based on our results, we can support this theory, as not only bulk SOC but also bulk black carbon disappears in the long-term, seemingly contradicting a stabilization of black carbon in the fine fraction of the Gartow soil, which is reasonable, as it is dominated by sand. In contrast to that, Cooper et al. (2020) demonstrated that only high biochar application amounts of 31.5 Mg ha^{-1} could stabilize SOC in the stable $<$0.053 mm fraction, both in 0–10 cm and 10–30 cm soil depth, six years after application. This corroborates our findings that only high amounts of biochar showed significant effects on SOC sequestration after eleven years (Table S1).

4.1.2. Influence of biochar properties on SOC stock changes

Other dominant factors influencing amendment-induced SOC sequestration are the biochar properties. The biochar used at the Bayreuth site was made of wood and showed a higher content of C, black carbon, and a higher C/N ratio than the biochar used at the Gartow site, which was made of green cuts. The C and N content in biochar, along with C/N ratio, are critical factors determining the stability of biochar and its ability to contribute to SOC build-up (Liu et al., 2016), with higher biochar C contents leading to more C input and therefore enhanced SOC sequestration potential. Conversely, OSA with higher N contents, resulting in lower C/N ratios, may lead to an increase in soil respiration and CO_2 emissions due to the greater availability of N and enhanced rates of microbial C mineralization (Huang et al., 2004; Zou et al., 2004). Another decisive property to describe biochar stability is the H/C ratio (Schimmelpfennig and Glaser, 2012; Budai et al., 2013). The H/C ratio is an indicator for the aromaticity of biochar. Compared to uncharred biomass, which typically possesses higher H/C ratios, biochar with low ratios is expected to be more stable in the long-term (Budai et al., 2013). The fact that the biochar used at both sites showed a high stability based on the low H/C ratio results indicated that the stability of biochar must also be assessed in the context of its intended use and location.

4.2. Long-term effects of different biochar treatments on black carbon stocks

Little is known about the long-term fate of black carbon in agricultural soils after the addition of biochar. We used black carbon as a molecular marker for the amount and quality of biochar in both soils. However, the amount of black carbon and biochar is not identical due to a conversion factor of 2.27 that we used to multiply the sum of BPCA into biochar equivalents (Glaser et al., 1998). For higher accuracy, individual conversion factors for individual fresh and aged biochar should be determined in the future, which was beyond the scope of this study. Nevertheless, differing black carbon stocks can be used as a relative indicator for altering biochar stability because it specifically traces the stable polyaromatic backbone of biochar (Glaser et al., 1998). Significant effects of biochar addition on the black carbon stocks in 2021 were only observable, when at least 31.5 Mg ha^{-1} of biochar was added (Table S2). By looking at the black carbon time series at the Bayreuth and Gartow sites (Fig. 2), it could be seen that both the low amount and high amount of biochar were affected by dissipation; in Bayreuth, however, much weaker and with large data variability.

Not just the black carbon stock itself can be used as an indicator for altering biochar stability, but also the relative contribution of individual BPCA. Larger shares of B5CA and B6CA reflect higher degrees of aromatic condensation (Glaser et al., 1998), stronger oxidation resistance and are often related to higher pyrolysis temperature (Chang et al., 2019), and thus higher stability. The relative contribution of B5CA and B6CA increased between 2010 and 2021 in all treatments containing high biochar amounts at the Bayreuth site, while, apart from the biochar + digestate treatment, all treatments containing high biochar amounts of the Gartow field experiment slightly lost higher aromatic BPCA (Fig. 3). In the case of the Bayreuth field experiment, this suggests that black carbon stocks may be heading towards a long-term steady state, as the more stable compounds may prevail in the long-term.

At the Gartow site, however, the slight loss of higher aromatic compounds was probably not due to biochar decay, since the H/C ratio indicated a high stability but was more likely to be related to the sandy soil texture in Gartow and the associated lack of physical stabilization and protection against biochar movement (Polifka et al., 2018), e.g., through vertical transport. This finding agrees with Wang et al. (2023), who found subsoil accumulation of B5CA and B6CA compounds after the use of biochar.

4.2.1. Influence of biochar oxidation and metabolization on black carbon stocks

During biochar aging, oxidation processes typically decline biochar C compounds (Li et al., 2019). These oxidation processes may lead to biochar degradation, but the adsorption of organic materials and inorganic materials increase the protection of biochar and thus the stability of biochar's aromatic backbone (Nguyen et al., 2008; Hagemann et al., 2017). Such an organic coating is typical for aged co-composted biochar particles (Hagemann et al., 2017).

At the Bayreuth site, the co-composted biochar treatment affected black carbon stocks similarly like the pristine biochar and biochar mixed

with compost did (Table S2) and showed a comparable BPCA pattern over time (Fig. 3). Therefore, there was no evidence for enhanced biochar oxidation due to compost-induced increase of microbial activity. Higher overall black carbon stocks of the co-composted biochar treatment suggests that the organic coating associated with co-composted biochar particles might have led to biochar stabilization (Table S3), which could, however, not be statistically corroborated, since there was no significant difference between the biochar-containing OSA treatments (Table S2).

It could not be ruled out that biochar metabolization led to molecules not visible by our analytical procedure, such as free BPCA as biochar metabolites, which may be stabilized into soil organic matter (Di Rauso et al., 2018). Evidence of such stabilization was observed in the diminishing quantities of biochar over time, as suggested by black carbon analysis, alongside an increase in the relative presence of more highly aromatic black carbon compounds (Fig. 3), with SOC levels remaining relatively stable (Fig. 2). Co-composting with biochar significantly improves the accessibility of nutrients on the biochar's surface (Hagemann et al., 2017), potentially facilitating co-metabolism. Once these surface nutrients are depleted, microorganisms begin to "mine" for new sources of N and P, while releasing enzymes that break down organic matter under stress (Whitman et al., 2015). This co-metabolic degradation becomes crucial when there is no mineral-organic interaction to stabilize the soil, which can be the case in very sandy soil environments (Polifka et al., 2018). In soils with low clay content, like in Gartow, the loss of C following the addition of large amounts of biochar can reach up to 20 %, a significantly higher rate than in soils with high clay content (Wang et al., 2016). In the Gartow experiment, fermented digestate combined with 40 Mg ha^{-1} of biochar led to significantly higher black carbon stocks (Table S3). Additional fermentation of digestate reduces the amount of easily degradable organic matter and thus the availability of nutrients, which could have diminished co-metabolic degradation of biochar.

4.2.2. *Influence of lateral and/or vertical biochar particle transport on black carbon stocks*

Biochar particles are usually more susceptible to vertical and/or lateral transport than mineral soil particles. This movement is largely influenced by water flow, wind, and soil macrofauna activity. The downward movement of biochar is particularly influenced by tillage and the physical structure of the soil (Obia et al., 2017), the amount of rainfall and hydraulic conductivity (Major et al., 2010; Obia et al., 2017), as well as bioturbation (Major et al., 2010). Obia et al. (2017) found that between 9 and 19 % of the total loss of biochar in general is due to vertical transport. Downward movement of biochar with time could be observed in both experiments (Table 4). Black carbon stocks significantly increased in the 10–30 cm layer while biochar dissipated in the 0–10 cm layer. As biochar moves into deeper soil layers, it continues to participate in carbon sequestration. We found that SOC stocks in the subsoil layer 10–30 cm increased with progressing time, confirming this theory. Biochar particles can enhance C sequestration even additionally through the formation of inorganic carbon in the subsoil (Wang et al., 2023).

Lateral biochar movement, which is predominantly due to wind erosion and surface water runoff, is also an important transport pathway and can account for 20 to 53 % of total dissipation (Major et al., 2010). To quantify the impact of lateral transport of biochar on the experimental results, we looked at potential pathways (Figs. S3 and S4). We compared SOC and black carbon stocks between plots that received no biochar at all and plots that received high amounts of biochar in both experiments. At the Bayreuth site, nearly all biochar-free-plots adjacent to a plot which received high amounts of biochar (31.5 Mg ha^{-1}) exhibited increases in SOC and black carbon stocks over time (Fig. S3a and b), indicating lateral transport. In Gartow, similar lateral movement could not be observed. SOC and black carbon stocks showed no specific trend between biochar-free-plots adjacent to a plot which received high amounts of biochar (40 Mg ha^{-1}). This could indicate that vertical biochar particle transport is more important in a very sandy soil matrix.

In order to investigate this effect systematically, quantitatively, and statistically, an experimental design focusing on transport dynamics is needed, or systematic sampling outside the biochar plots, at increasing distances with sufficient repetition. As such biochar particle migration takes time, we expect on the one hand to find significant amounts of biochar outside the experiment plots and on the other hand, the SOC stocks to increase in deeper soil regions in the long-term, which should be studied in the future. To date, there is a lack of long-term field experiments that could deliver proof of concept.

5. Conclusion

So far, there is lack of evidence on the fate of SOC and black carbon stocks under field experiment conditions, on a decadal time scale under realistic field conditions. Moreover, previous approaches trying to quantify SOC stock differences and biochar loss and migration rates are characterized by high uncertainties, have not been tested in more than one agroecosystem and are not based on long-term observations. The bottom line is, therefore, that it is difficult to generalize SOC and biochar dynamics. In this study, we present results of long-term biochar field experiments, conducted in two contrasting agroecosystems in Germany.

Our study indicates that it depends on soil and biochar properties such as soil texture and the black carbon content of the biochar, whether SOC stocks are stable in the long-term and biochar dissipation can be mitigated. Under loamy soil conditions and with the usage of C-rich wood-based biochar, the initial SOC stock increases were stable over a

Table 4
Median soil organic carbon (SOC) stocks and black carbon (BC) stocks of the organic soil amendments containing of high biochar amounts (31.5 Mg ha^{-1} and 40 Mg ha^{-1}) in two soil depths 0–10 cm and 10–30 cm. SE = standard error. Different letters indicate significant differences between the years.

	Soil depth											
	0–10 cm						10–30 cm					
	SOC stocks±SE			BC stocks±SE			SOC stocks±SE			BC stocks±SE		
	Mg ha^{-1}											
Bayreuth												
Year												
2010	52.80	±	1.92a	8.54	±	0.35a	39.63	±	1.69a	3.25	±	0.80a
2011	56.24	±	2.08a	12.39	±	1.37b	38.08	±	3.35a	2.80	±	0.57a
2013	30.45	±	1.17b	2.79	±	0.67c	51.58	±	2.08b	7.36	±	0.65b
Gartow												
Year												
2012	34.27	±	4.31a	7.27	±	1.63a	15.99	±	0.45a	0.28	±	0.03a
2014	24.73	±	2.41a	1.06	±	0.69b	15.03	±	0.86a	1.65	±	0.86b
2016	17.08	±	1.39b	2.33	±	0.27b	25.31	±	1.90b	3.11	±	0.47b

time frame of eleven years and thus SOC sequestration was confirmed. In contrast, the observations on the sandy soil made over nine years and under the use of biochar with a lower C/N ratio and a lower content of stable poly-condensed aromatic moieties were characterized by large SOC and black carbon losses, seemingly related to lacking physical protection and vertical biochar particle transport. According to black carbon stock results, considerable biochar loss was observed in both soils, which may be related to multiple dissipation processes occurring at the same time, such as oxidation and/or co-metabolic decomposition, or vertical and lateral particle transport. However, persisting high SOC levels at the Bayreuth site despite decreasing black carbon levels indicate biochar stabilization even if black carbon detection was not always possible. This study was able to demonstrate that the re-sampling of long-term biochar field experiments provided insights into the long-term behavior of SOC stocks and biochar. The observed dynamics should be further validated in future sampling.

Additionally, future studies should disentangle the different dissipation pathways and their impact on SOC sequestration. More experimental proof is necessary on how the long-term fate of biochar induced SOC stock increases are influenced by biochar properties and the respective agroecosystem, with unique soil properties and agricultural management decisions. Without a broad empirical basis, these findings are not transferable into agronomic practice.

CRediT authorship contribution statement

Arthur Gross: Writing – original draft, Visualization, Formal analysis, Conceptualization. **Tobias Bromm:** Writing – review & editing, Validation, Formal analysis. **Steven Polifka:** Writing – review & editing, Validation, Investigation. **Daniel Fischer:** Writing – review & editing, Validation, Investigation. **Bruno Glaser:** Writing – review & editing, Validation, Supervision, Investigation, Conceptualization.

Declaration of competing interest

The authors have no relevant financial or non-financial interests to disclose.

Data availability

Data will be made available on request.

Acknowledgements

The authors acknowledge the financial support by the European Union [Grant No. 101059546], the Graduate Scholarship Program of Saxony-Anhalt and the Open Access Publication Fund of the Martin Luther University Halle-Wittenberg. We also thank the helpers who conducted field and laboratory work: C. Heinrich, H. Maennicke, Y. Mayer, K. Wiedner, A. Boritzki, C. Krenkewitz and countless student helpers. We would particularly like to thank the "Landwirtschaftlichen Lehranstalten" in Bayreuth and Graf Fried von Bernstorff for their cooperation and provision of arable land.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2024.176340.

References

Alvarenga, P., Carneiro, J.P., Fangueiro, D., Cordovil, C.M.d.S., Bernal, M.P., 2020. Managing organic amendments in agroecosystems to enhance soil carbon storage and mitigate climate change. In: Climate Change and Soil Interactions. Elsevier, pp. 89–141. https://doi.org/10.1016/B978-0-12-818032-7.00005-9.

Bates, D., Mächler, M., Bolker, B., Walker, S., 2015. Fitting linear mixed-effects models using lme4. J. Stat. Softw. 67 (1). https://doi.org/10.18637/jss.v067.i01.

Berhane, M., Xu, M., Liang, Z., Shi, J., Wei, G., Tian, X., 2020. Effects of long-term straw return on soil organic carbon storage and sequestration rate in North China upland crops: a meta-analysis. Glob. Chang. Biol. 26 (4), 2686–2701. https://doi.org/10.1111/gcb.15018.

Blanco-Canqui, H., Laird, D.A., Heaton, E.A., Rathke, S., Acharya, B.S., 2020. Soil carbon increased by twice the amount of biochar carbon applied after 6 years: field evidence of negative priming. GCB Bioenergy 12 (4), 240–251. https://doi.org/10.1111/gcbb.12665.

Brodowski, S., Amelung, W., Haumaier, L., Abetz, C., Zech, W., 2005. Morphological and chemical properties of black carbon in physical soil fractions as revealed by scanning electron microscopy and energy-dispersive X-ray spectroscopy. Geoderma 128 (1), 116–129. https://doi.org/10.1016/j.geoderma.2004.12.019.

Bruun, S., Clauson-Kaas, S., Bobuľská, L., Thomsen, I.K., 2014. Carbon dioxide emissions from biochar in soil: role of clay, microorganisms and carbonates. Eur. J. Soil Sci. 65, 52–59. https://doi.org/10.1111/ejss.12073.

Budai, A., Zimmerman, A.R., Cowie, A.L., Webber, J.B.W., Singh, B.P., Glaser, B., Joseph, S., 2013. Biochar Carbon Stability Test Method: An Assessment of Methods to Determine Biochar Carbon Stability. International Biochar Initiative.

Chang, Z., Tian, L., Zhang, J., Zhao, Q., Li, F., Wu, M., Pan, B., 2019. Combining bulk characterization and benzene polycarboxylic acid molecular markers to describe biochar properties. Chemosphere 227, 381–388. https://doi.org/10.1016/j.chemosphere.2019.03.164.

Cooper, J., Greenberg, I., Ludwig, B., Hippich, L., Fischer, D., Glaser, B., Kaiser, M., 2020. Effect of biochar and compost on soil properties and organic matter in aggregate size fractions under field conditions. Agric. Ecosyst. Environ. 295, 106882. https://doi.org/10.1016/j.agee.2020.106882.

De La Rosa, J.M., Rosado, M., Paneque, M., Miller, A.Z., Knicker, H., 2018. Effects of aging under field conditions on biochar structure and composition: implications for biochar stability in soils. Sci. Total Environ. 613–614, 969–976. https://doi.org/10.1016/j.scitotenv.2017.09.124.

Di Rauso, Simeone G., Benesch, M., Glaser, B., 2018. Degradation products of polycondensed aromatic moieties (black carbon or pyrogenic carbon) in soil: methodological improvements and comparison to contemporary black carbon concentrations. J. Plant Nutr. Soil Sci. 181 (5), 714–720. https://doi.org/10.1002/jpln.201800079.

Ding, F., Van Zwieten, L., Zhang, W., Weng, Z., Shi, S., Wang, J., Meng, J., 2018. A meta-analysis and critical evaluation of influencing factors on soil carbon priming following biochar amendment. J. Soils Sediments 18, 1507–1517. https://doi.org/10.1007/s11368-017-1899-6.

FAO, 2019. Measuring and Modelling Soil Carbon Stocks and Stock Changes in Livestock Production Systems: Guidelines for Assessment (Version 1): Livestock Environmental Assessment and Performance (LEAP) Partnership. Rome.

FAO and ITPS, 2015. Status of the world's Soil Resources: Main Report. FAO, Rome.

Fischer, D., Glaser, B., 2012. Synergisms between compost and biochar for sustainable soil amelioration. In: Kumar, S. (Ed.), Management of Organic Waste. InTech. https://doi.org/10.5772/31200.

Glaser, B., 1999. Eigenschaften und Stabilität des Humuskörpers der „Indianerschwarzerden. Amazoniens, Bayreuther Bodenkundliche Berichte, Bayreuth.

Glaser, B., Haumaier, L., Guggenberger, G., Zech, W., 1998. Black carbon in soils: the use of benzenecarboxylic acids as specific markers. Org. Geochem. 29 (4), 811–819. https://doi.org/10.1016/S0146-6380(98)00194-6.

Gross, A., Glaser, B., 2021. Meta-analysis on how manure application changes soil organic carbon storage. Sci. Rep. 11 (1), 5516. https://doi.org/10.1038/s41598-021-82739-7.

Glaser, B., Wiedner, K., Seelig, S., Schmidt, H.-P., Gerber, H., 2015. Biochar organic fertilizers from natural resources as substitute for mineral fertilizers. Agron. Sustain. Dev. 35, 667–678. https://doi.org/10.1007/s13593-014-0251-4.

Greenberg, I., Kaiser, M., Polifka, S., Wiedner, K., Glaser, B., Ludwig, B., 2019. The effect of biochar with biogas digestate or mineral fertilizer on fertility, aggregation and organic carbon content of a sandy soil: Results of a temperate field experiment. J. Plant Nutr. Soil Sci. 182, 824–835. https://doi.org/10.1002/jpln.201800496.

Gross, A., Bromm, T., Glaser, B., 2021. Soil organic carbon sequestration after biochar application: a global meta-analysis. Agronomy 11 (12), 2474. https://doi.org/10.3390/agronomy11122474.

Guo, F., Wang, C., Wang, S., Zhao, X., Li, G., Sun, Z., 2024. The native SOC increase in woodland and lawn soil amended with biochar surpassed greenhouse — A seven-year field trial. Sci. Total. Environ. 907, 167924. https://doi.org/10.1016/j.scitotenv.2023.167924.

Hagemann, N., Joseph, S., Schmidt, H.-P., Kammann, C., Harter, J., Borch, T., Young, R. A., Young, R.B., Varga, K., Taherymoosavi, S., Elliott, K.W., McKenna, A.M., Albu, Mihaela, Albu, M., Mayrhofer, Claudia, Mayrhofer, C., Mayrhofer, C., Obst, M., Conte, P., Dieguez-Alonso, A., Orsetti, S., Subdiaga, E., Behrens, S., Kappler, A., 2017. Organic coating on biochar explains its nutrient retention and stimulation of soil fertility. Nat. Commun. 8 (1), 1089. https://doi.org/10.1038/s41467-017-01123-0.

Han, P., Zhang, W., Wang, G., Sun, W., Huang, Y., 2016. Changes in soil organic carbon in croplands subjected to fertilizer management: a global meta-analysis. Sci. Rep. 6 (1), 27199. https://doi.org/10.1038/srep27199.

Huang, Y., Zou, J., Zheng, X., Wang, Y., Xu, X., 2004. Nitrous oxide emissions as influenced by amendment of plant residues with different C: N ratios. Soil Biol. Biochem. 36 (6), 973–981.

Huang, Y., Tao, B., Lal, R., Lorenz, K., Jacinthe, P.-A., Shrestha, R.K., Bai, X., Singh, M.P., Lindsey, L.E., Ren, W., 2023. A global synthesis of biochar's sustainability in climate-smart agriculture - evidence from field and laboratory experiments. Renew. Sustain. Energy Rev. 172, 113042. https://doi.org/10.1016/j.rser.2022.113042.

Kammann, C.I., Schmidt, H.-P., Messerschmidt, N., Linsel, S., Steffens, D., Müller, C., Koyro, H.-W., Conte, P., Joseph, S., 2015. Plant growth improvement mediated by nitrate capture in co-composted biochar. Sci. Rep. 5, 11080. https://doi.org/10.1038/srep11080.

Kenward, M.G., Roger, J.H., 1997. Small sample inference for fixed effects from restricted maximum likelihood. Biometrics 53 (3), 983. https://doi.org/10.2307/2533558.

Knicker, H., 2011. Pyrogenic organic matter in soil: its origin and occurrence, its chemistry and survival in soil environments. Quat. Int. 243 (2), 251–263. https://doi.org/10.1016/j.quaint.2011.02.037.

Kuzyakov, Y., Bogomolova, I., Glaser, B., 2014. Biochar stability in soil: decomposition during eight years and transformation as assessed by compound-specific 14C analysis. Soil Biol. Biochem. 70, 229–236. https://doi.org/10.1016/j.soilbio.2013.12.021.

Lal, R., 2008. Carbon sequestration. Philos. Trans. R. Soc., B 363 (1492), 815–830. https://doi.org/10.1098/rstb.2007.2185.

Lal, R., 2018. Digging deeper: a holistic perspective of factors affecting soil organic carbon sequestration in agroecosystems. Glob. Chang. Biol. 24 (8), 3285–3301. https://doi.org/10.1111/gcb.14054.

Lal, R., Follett, R.F., Stewart, B.A., Kimble, J.M., 2007. Soil carbon sequestration to mitigate climate change and advance food security. Soil Sci. 172 (12), 943–956. https://doi.org/10.1097/ss.0b013e31815cc498.

Lal, R., Negassa, W., Lorenz, K., 2015. Carbon sequestration in soil. Curr. Opin. Environ. Sustain. 15, 79–86. https://doi.org/10.1016/j.cosust.2015.09.002.

Lehmann, J., Kleber, M., 2015. The contentious nature of soil organic matter. Nature 528 (7580), 60–68. https://doi.org/10.1038/nature16069.

Lehmann, J., Abiven, S., Azzi, E., Fang, Y., Singh, B.P., Sohi, S., Sundberg, C., Woolf, D., Zimmerman, A.R., 2024. Persistence of biochar. In: Biochar for Environmental Management. Routledge, London, pp. 277–311. https://doi.org/10.4324/9781003297673-11.

Lenth, R., Bolker, B., Buerkner, P., 2023. Emmeans: Estimated Marginal Means.

Li, H., Lu, X., Xu, Y., Liu, H., 2019. How close is artificial biochar aging to natural biochar aging in fields? A meta-analysis. Geoderma 352, 96–103. https://doi.org/10.1016/j.geoderma.2019.06.006.

Liu, S., Zhang, Y., Zong, Y., Hu, Z., Wu, S., Zhou, J., Jin, Y., Zou, J., 2016. Response of soil carbon dioxide fluxes, soil organic carbon and microbial biomass carbon to biochar amendment: a meta-analysis. GCB Bioenergy 8 (2), 392–406. https://doi.org/10.1111/gcbb.12265.

Maestrini, B., Nannipieri, P., Abiven, S., 2015. A meta-analysis on pyrogenic organic matter induced priming effect. GCB Bioenergy 7 (4), 577–590. https://doi.org/10.1111/gcbb.12194.

Major, J., Lehmann, J., Rondon, M., Goodale, C., 2010. Fate of soil-applied black carbon: downward migration, leaching and soil respiration. Glob. Chang. Biol. 16 (4), 1366–1379. https://doi.org/10.1111/j.1365-2486.2009.02044.x.

Men, M., Peng, Z., Hao, X., Yu, Z., 2008. Investigation on Pedotransfer function for estimating soil bulk density in Hebei province. Chin. J. Soil Sci. 1, 20.

Meyer, S., Bright, R.M., Fischer, D., Schulz, H., Glaser, B., 2012. Albedo impact on the suitability of biochar systems to mitigate global warming. Environ. Sci. Technol. 46 (22), 12726–12734. https://doi.org/10.1021/es302302g.

Mukome, F., Parikh, S., 2015. Chemical, Physical, and Surface Characterization of Biochar. In: Biochar: Production, Characterization, and Applications.

Nannipieri, P., Trasar-Cepeda, C., Dick, R.P., 2018. Soil enzyme activity: a brief history and biochemistry as a basis for appropriate interpretations and meta-analysis. Biol. Fertil. Soils 54 (1), 11–19. https://doi.org/10.1007/s00374-017-1245-6.

Nguyen, B.T., Lehmann, J., Kinyangi, J., Smernik, R.J., Riha, S.J., Engelhard, M.H., 2008. Long-term black carbon dynamics in cultivated soil. Biogeochemistry 89 (3), 163–176. https://doi.org/10.1007/s10533-008-9220-9.

Obia, A., Børresen, T., Martinsen, V., Cornelissen, G., Mulder, J., 2017. Vertical and lateral transport of biochar in light-textured tropical soils. Soil Tillage Res. 165, 34–40. https://doi.org/10.1016/j.still.2016.07.016.

Piepho, H.P., Büchse, A., Emrich, K., 2003. A hitchhiker's guide to mixed models for randomized experiments. J. Agron. Crop Sci. 189 (5), 310–322. https://doi.org/10.1046/j.1439-037X.2003.00049.x.

Polifka, S., Wiedner, K., Glaser, B., 2018. Increased CO2 fluxes from a sandy Cambisol under agricultural use in the Wendland region, northern Germany, three years after biochar substrates application. GCB Bioenergy 10 (7), 432–443. https://doi.org/10.1111/gcbb.12517.

R Core Team, 2021. R: A language and environment for statistical computing.

Rasul, M., Cho, J., Shin, H.-S., Hur, J., 2022. Biochar-induced priming effects in soil via modifying the status of soil organic matter and microflora: a review. Sci. Total Environ. 805, 150304. https://doi.org/10.1016/j.scitotenv.2021.150304.

Rumpel, C., Amiraslani, F., Chenu, C., Garcia Cardenas, M., Kaonga, M., Koutika, L.-S., Ladha, J., Madari, B., Shirato, Y., Smith, P., Soudi, B., Soussana, J.-F., Whitehead, D., Wollenberg, E., 2020. The 4p1000 initiative: opportunities, limitations and challenges for implementing soil organic carbon sequestration as a sustainable development strategy. Ambio 49 (1), 350–360. https://doi.org/10.1007/s13280-019-01165-2.

Schimmelpfennig, S., Glaser, B., 2012. One step forward toward characterization: some important material properties to distinguish biochars. J. Environ. Qual. 41 (4), 1001–1013. https://doi.org/10.2134/jeq2011.0146.

Spokas, K.A., Reicosky, D.C., 2009. Impacts of sixteen different biochars on soil greenhouse gas production. AES 3.

Spokas, K.A., Novak, J.M., Masiello, C.A., Johnson, M.G., Colosky, E.C., Ippolito, J.A., Trigo, C., 2014. Physical disintegration of biochar: an overlooked process. Environ. Sci. Technol. Lett. 1, 326–332. https://doi.org/10.1021/ez500199t.

Tumwesigye, W., Bedadi, B., Atwiine, J., 2021. Effect of climate change on soil health and implications on food security: a review. International Research Journal of Multidisciplinary Technovation 38–46. https://doi.org/10.34256/irjmt2136.

UN, 2015. World Population Prospects: The 2015 Revision, Key Findings and Advance Tables.: Working Paper No. ESA/P/WP.241. New York.

Wang, J., Xiong, Z., Kuzyakov, Y., 2016. Biochar stability in soil: meta-analysis of decomposition and priming effects. GCB Bioenergy 8 (3), 512–523. https://doi.org/10.1111/gcbb.12266.

Wang, Y., Joseph, S., Wang, X., Weng, Z.H., Mitchell, D.R.G., Nancarrow, M., Taherymoosavi, S., Munroe, P., Li, G., Lin, Q., Chen, Q., Flury, M., Cowie, A., Husson, O., Van Zwieten, L., Kuzyakov, Y., Lehmann, J., Li, B., Shang, J., 2023. Inducing inorganic carbon accrual in subsoil through biochar application on calcareous topsoil. Environ. Sci. Technol. 57 (4), 1837–1847. https://doi.org/10.1021/acs.est.2c06419.

Whitman, T., Singh, B.P., Zimmerman, A.R., Lehmann, J., Joseph, S., 2015. Priming effects in biochar-amended soils: implications of biochar-soil organic matter interactions for carbon storage. Biochar for environmental management: Science, technology and implementation 2, 455–488.

Yang, X.Y., Chang, K.-H., Kim, Y.J., Zhang, J., Yoo, G., 2019. Effects of different biochar amendments on carbon loss and leachate characterization from an agricultural soil. Chemosphere 226, 625–635. https://doi.org/10.1016/j.chemosphere.2019.03.085.

Zhang, L., Xiang, Y., Jing, Y., Zhang, R., 2019. Biochar amendment effects on the activities of soil carbon, nitrogen, and phosphorus hydrolytic enzymes: a meta-analysis. Environ. Sci. Pollut. Res. 26 (22), 22990–23001. https://doi.org/10.1007/s11356-019-05604-1.

Zong, Y., Wang, Y., Sheng, Y., Wu, C., Lu, S., 2018. Ameliorating soil acidity and physical properties of two contrasting texture Ultisols with wastewater sludge biochar. Environ. Sci. Pollut. Res. 25 (26), 25726–25733. https://doi.org/10.1007/s11356-017-9509-0.

Zou, J., Huang, Y., Zong, L., Zheng, X., Wang, Y., 2004. Carbon dioxide, nitrous oxide and methane emissions from a rice-winter wheat rotation system as affected by crop residue incorporation and temperature. Adv. Atmos. Sci. 21 (69), 1–698. https://doi.org/10.1007/BF02916366.