RESEARCH REVIEW

Biochar stability in soil: meta-analysis of decomposition and priming effects

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Abstract

The stability and decomposition of biochar are fundamental to understand its persistence in soil, its contribution to carbon (C) sequestration, and thus its role in the global C cycle. Our current knowledge about the degradability of biochar, however, is limited. Using 128 observations of biochar-derived CO_2 from 24 studies with stable (^{13}C) and radioactive (^{14}C) carbon isotopes, we meta-analyzed the biochar decomposition in soil and estimated its mean residence time (MRT). The decomposed amount of biochar increased logarithmically with experimental duration, and the decomposition rate decreased with time. The biochar decomposition rate varied significantly with experimental duration, feedstock, pyrolysis temperature, and soil clay content. The MRTs of labile and recalcitrant biochar C pools were estimated to be about 108 days and 556 years with pool sizes of 3% and 97%, respectively. These results show that only a small part of biochar is bioavailable and that the remaining 97% contribute directly to long-term C sequestration in soil. The second database (116 observations from 21 studies) was used to evaluate the priming effects after biochar addition. Biochar slightly retarded the mineralization of soil organic matter (SOM; overall mean: −3.8%, 95% CI = −8.1–0.8%) compared to the soil without biochar addition. Significant negative priming was common for studies with a duration shorter than half a year (−8.6%), crop-derived biochar (−20.3%), fast pyrolysis (−18.9%), the lowest pyrolysis temperature (−18.5%), and small application amounts (−11.9%). In contrast, biochar addition to sandy soils strongly stimulated SOM mineralization by 20.8%. This indicates that biochar stimulates microbial activities especially in soils with low fertility. Furthermore, abiotic and biotic processes, as well as the characteristics of biochar and soils, affecting biochar decomposition are discussed. We conclude that biochar can persist in soils on a centennial scale and that it has a positive effect on SOM dynamics and thus on C sequestration.

Keywords: black carbon, C sequestration, climate change, priming effect, pyrogenic organic matter, soil respiration

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Introduction

Biochar, the carbonaceous residue of pyrolyzed organic materials under low oxygen conditions, has gained increasing attention in the last decade. Biochar is used for increasing soil carbon (C) sequestration (Lehmann *et al.*, 2006; Schmidt *et al.*, 2011), soil remediation (Ahmad *et al.*, 2014; Zhang & Ok, 2014), greenhouse gas emissions mitigation (Woolf *et al.*, 2010; Gurwick *et al.*, 2013), as well as improving soil fertility and crop yields (Jeffery *et al.*, 2011; Biederman & Harpole, 2013). Notably, its importance as a supply-side mitigation option is for the first time highlighted and summarized in the latest Intergovernmental Panel on Climate Change report (Smith *et al.*, 2014).

A recent modeling study has demonstrated that sustainable biochar production could help reduce net greenhouse gas emissions by a maximum of 1.8 Pg CO_2-C equivalent annually without penalizing ecosystem stability and food security; the inert C of biochar is the largest contributor because of its highly stable characteristic (Woolf *et al.*, 2010). The biochemical stability of biochar is crucial mainly due to its longevity in soil after application and its long-term maintenance of fertility (Glaser *et al.*, 2002; Lehmann *et al.*, 2009). It remains unclear, however, to what extent biochar is degraded and what its concomitant effects on native soil organic matter (SOM) turnover and other cascading impacts are (Lehmann *et al.*, 2011; Ameloot *et al.*, 2013; Lorenz & Lal, 2014). Although the available studies have reviewed the fate of biochar in various environments (Schmidt & Noack, 2000; Forbes *et al.*, 2006; Preston &

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Schmidt, 2006; Knicker, 2007, 2011), the current scientific understanding of biochar stability and persistence in soil remains sparse and incomplete. There are two reasons for this lack of knowledge about biochar decomposition in soil. Firstly, the contribution of biochar to total CO_2 efflux from soil is too small to differentiate it from the background of high CO_2 efflux from other sources, that is, SOM, dead plant residues, DOC (Kuzyakov et al., 2009). Secondly, without information on the initial stock or input of biochar or other pyrogenic carbon in soils, any estimation of biochar decomposition based on its content in soil may be biased. To some extent, the results derived from such approaches as chronosequences or ^{14}C dating are thus biased (Marschner et al., 2008; Ohlson et al., 2009; Singh et al., 2012a).

Improved approaches, such as using benzenepolycarboxylic acids (BPCAs) as molecular markers of biochar, have been successfully used to quantify the amount of biochar and evaluate its sources in soils (Glaser et al., 1998; Brodowski et al., 2005; Hammes et al., 2008; Schneider et al., 2011). Although these approaches help assess potential sources of biochar in soil and the contribution of biochar compounds to SOM, they fail to quantitatively evaluate biochar decomposition rates and dynamics in soils as BPCAs are only part of biochar C. This makes the assessment of biochar stability in soil impossible using these and the above-described approaches.

Ten years ago, a new approach based on application of [14]C- (and/or ^{13}C-labeled) biochar was suggested to trace its turnover and transformation products against the background of other CO_2 sources from soil (Kuzyakov et al., 2009, 2014). Currently, changing biochar input from C3 to C4 plant material or vice versa or also applying artificially ^{13}C-enriched or ^{13}C-depleted biochar was introduced to estimate its turnover in various soils (e.g., Glaser & Knorr, 2008; Bruun et al., 2014; Singh et al., 2014). Compared with previously used methods to assess biochar turnover, these ^{13}C and ^{14}C techniques improve our understanding of biochar dynamics in soils and their cascading effects on ecosystem processes.

Nonetheless, the extent of biochar decomposition and its mean residence time (MRT) in soils means its stability remains nearly unknown. The overall objective of this meta-analysis is therefore to synthesize those biochar decomposition studies in which ^{13}C or ^{14}C isotopes were used. We first collected the published studies and established a database on the magnitude and rates of biochar decomposition. This database contains 128 observations of biochar-derived CO_2 from 24 studies (Table S1). We then evaluated both the factors and processes affecting its degradation and stability. Next, we used this database to estimate the MRT of biochar in soil using the double exponential decay model. Finally, the effect of biochar addition on native SOM decomposition

(e.g., priming effect) was assessed by a meta-analysis based on the studies evaluating biochar stability.

Materials and methods

Data compilation

The synthesis was performed on published data of biochar decomposition collected using *ISI Web of Science* and *Google Scholar*. The following criteria were applied to select appropriate studies. (1) To reliably evaluate biochar decomposition in soil, we restricted the data collection to studies employing stable isotopic techniques (^{13}C natural abundance or ^{13}C labeling) or ^{14}C labeling to separate biochar-derived CO_2 from CO_2 derived from native SOM or other C sources (e.g., plant residues). (2) If more than one publication presented results from the same experiment, we selected data only from the studies with the longest experimental duration (Stewart et al., 2013; Fang et al., 2014a; Maestrini et al., 2014a). (3) The analysis was focused solely on biochar produced by pyrolyzing organic materials under dry conditions. Hence, the other types of carbonized biomass (e.g., hydrothermal char) were not considered (Malghani et al., 2013). (4) To avoid the confounding effects of temperature on biochar decomposition, we excluded incubation studies at temperatures exceeding 40 °C (Fang et al., 2014a). (5) A few studies were excluded that reported negative values of biochar decomposition because of high variation by application of ^{13}C natural abundance or because isotopic fractionation was not considered (Cross & Sohi, 2011). After these restrictions, data were extracted from 24 studies with 128 observations that reported biochar decomposition (Table S1). The main characteristics of included studies are presented in Table S1. Experimental factors potentially affecting biochar decomposition were summarized by a number of categorical variables: type of experiment, experimental duration, feedstock, pyrolysis type and temperature of biochar production, application amount, ash content, land use, as well as soil clay content (Table 1).

In addition, a meta-analysis was performed to explore the effect of biochar-induced priming on SOM mineralization. We restricted our database of biochar-induced priming effects on those studies that simultaneously investigated biochar decomposition as described above and Jones et al. (2011). This yielded a database consisted of 116 observations from 21 studies, which was used to evaluate the priming effect after biochar addition (Table S1).

Statistical analysis

Most of the data included in our analysis were extracted from tables and figures in published studies. Few data not presented in the literature were obtained via personal communication (Farrell et al., 2013). The data presented in graphs were extracted by digitizing the figures using G3DATA software (http://www.frantz.fi/software/g3data.php). When means and standard errors (SE) were reported, the standard deviations (SD) were calculated as: $SD = SE\sqrt{n}$, where n is the number of replicates. All values of biochar decomposed

Table 1 Statistical results of comparisons for biochar decomposition rate (% day^{-1}) by Kruskal–Wallis ANOVA and for the weighted response ratios of the priming effect response to biochar addition by chi-square test among groups for selected categorical variables

Categorical variable	Group	Biochar decomposition rate		Priming effect	
		n. obs	Kruskal–Wallis test	n. obs	Chi-square test
Type of experiment	Incubation	121	0.59	113	0.37
	Field	7		3	
Experimental duration (year)	<0.5	55	**37.85*****	59	7.07
	0.5–1	8		5	
	1–2	46		37	
	>3	19		15	
Feedstock	Crop	51	**32.56*****	48	**31.99*****
	Wood	44		43	
	Grass	28		20	
	Manure	4		4	
Pyrolysis type	Slow	108	0.26	96	**14.21*****
	Fast	20		20	
Pyrolysis temperature (°C)	200–375	22	**34.53*****	17	**14.10****
	400–475	41		33	
	500–550	48		56	
	600–700	11		6	
	1200	6		4	
Ash content (%)	<20	21	0.06	22	**6.37***
	>20	22		20	
Application amount (%)	0.1–1	50	3.62	38	**10.20****
	1.1–3	50		54	
	5–20	28		24	
Land use	Agriculture	103	1.16	96	0.71
	Forest	14		11	
	Other	11		9	
Soil clay content (%)	<10	13	**20.42*****	12	**27.14*****
	10–20	26		16	
	20–40	49		48	
	40–70	27		27	

Values in bold indicate significant levels at *$P < 0.05$, **$P < 0.01$ and ***$P < 0.001$.

amounts (% of added) were recalculated and expressed as percent per day, being referred to as the biochar decomposition rate. The Kruskal–Wallis one-way analysis of variance (ANOVA) was used to investigate differences in biochar decomposition rate between various groups of each categorical variable (Table 1). A nonparametric multiple comparison test (Dunn's test) was performed to compare the difference in the sum of ranks between the groups with the expected average difference.

The MRT of biochar for each study was calculated as a reciprocal of the decomposition rate. To estimate decomposition rates and MRTs of biochar pools in soil, a double first-order exponential decay model was used to fit the experimental data of the remaining amount of biochar against experimental duration using a least squares optimization routine (Jones et al., 2011):

$$y = a \times \exp\left(-k_1 \times t\right) + b \times \exp\left(-k_2 \times t\right)$$

where y is the amount of biochar remaining in the soil, t is time, a and b represent the size of labile and recalcitrant C pools of biochar, respectively, and k_1 and k_2 are the exponential coefficients for these two pools. The MRTs for labile and recalcitrant C pools of biochar were calculated as reciprocal of k_1 and k_2, respectively. These statistical analyses were performed using STATISTICA v.10 (StatSoft. Inc., Tulsa, OK, USA).

The meta-analysis followed the approach described by Hedges et al. (1999). We used the natural log-transformed response ratio:

$$\ln RR = \ln(X_t/X_c)$$

where X_t and X_c are the means of SOM-derived CO_2 emission with and without biochar addition, respectively. The positive and negative log response ratios indicate SOM-derived CO_2 emissions increased and decreased after biochar addition, respectively. Similar to previous ecological studies, a mixed effects model was used with the assumption that differences among studies within a group are due to both sampling error and random variation (Gurevitch & Hedges, 1999). Considering studies where neither the SD nor the SE were available in the original papers, two weighting functions were used as follows: (i) each individual observation was weighted by the reciprocal of the pooled variance as is conventionally done in meta-analysis (Curtis & Wang, 1998); and (ii) the data were also weighted by experimental replication, using the function $F_N = (n_t \times n_c)/(n_t + n_c)$, where n_t and n_c represent the number of replicates for the treated and control groups, respectively (Adams et al., 1997). The total heterogeneity of effect sizes among studies (Q_T) is partitioned into within-group (Q_w) and between-group (Q_b) heterogeneity. The Q statistic approximately follows a chi-square distribution, which allows a significance test of the null hypothesis that all response ratios are equal. A Q_b larger than a critical value indicates that there has significant difference between groups. Mean effect sizes and 95% confidence intervals (CI) were generated using MetaWin 2.1 (Sinauer Associates Inc., Sunderland, MA, USA). The response ratio (RR) and CI of treatments presented were back-transformed from lnRR. For each case, biochar treatment was considered significant if the 95% CI of response ratio did not overlap with zero. Responses of groups were considered different if their 95% CIs did not overlap. Graphs were plotted in SIGMAPLOT v.12.0 (Systat Software Inc., San Jose, CA, USA).

Results and Discussion

The amounts and rates of biochar decomposition

The decomposed amounts of biochar increased logarithmically with experimental duration (Fig. 1, left), suggesting that part of biochar is biologically available

and can be slowly degraded by soil microorganisms. Nonetheless, the high uncertainty of the fitting curve does not enable predicting the decomposed amounts over periods longer than a few years. This finding is consistent with Hammes *et al.* (2008), who found that the proportions of less-condensed biochar C decreased when compared the quality of BPCA between archived and modern soil samples in a Russian steppe.

In contrast to the amounts, the decomposition rate of biochar showed a clear decrease pattern with experimental duration (Fig. 1, right). Overall, the biochar decomposition rate was calculated at a mean and median of 0.013% day^{-1} and 0.0046% day^{-1}, respectively. The experimental duration varied very strongly, ranging from 2 weeks to 8.5 years. All observations were divided for four subgroups based on the experimental duration. The mean value of biochar decomposition rate for studies lasting < 0.5 year was 0.023% day^{-1}, that is, more than four times faster than that from studies lasted longer than 1 year (0.005% day^{-1}; Fig. 2). Despite the major content of aromatic C, the results of short-term studies mainly represent the decomposition of the non- or less-condensed fraction of biochar. Results from several studies (Table S1) imply that this initially intensive decomposition disappeared after 2 years and was maintained at a very low level over prolonged periods (Kuzyakov *et al.*, 2009, 2014; Fang *et al.*, 2014a,b). Considering that the longest biochar decomposition study (8.5 years) is much shorter than its assessed MRT, all available data reflect the decomposition of only the most labile biochar compounds. The experimental duration is one of the most important factors affecting biochar decomposition rates in soils. The low determi-

nation coefficient, however, suggests that decomposition may also be affected by factors other than the duration of experiment.

Biochars derived from various sources have different chemical compositions that affect biological degradability (Lehmann *et al.*, 2011). The crop-derived biochar decomposed faster (mean: 0.025% day^{-1}) than other feedstocks investigated (Fig. 2). The grass-derived biochar is also characterized by a lower C content and is less condensed, meaning that its decomposition rate is expected to be comparable to crop-derived biochar (Hilscher *et al.*, 2009; Knicker, 2010). In our analysis, however, the biochar derived from grasses had a much lower value (mean: 0.007% day^{-1}) than those from crop. This inconsistency is probably because one-third of the group of grass-derived biochar studies was conducted with the longer period (Kuzyakov *et al.*, 2009, 2014). In addition, wood-derived biochar had the slowest decomposition rate (mean: 0.004% day^{-1}) as a result of its high C content (means: 66.4% vs. 59.8% for crop and 64.6% for grass; $P = 0.02$), corresponding to a higher aryl C content relative to both crop- and grass-derived biochars (Hilscher *et al.*, 2009; Singh & Cowie, 2014).

Increasing the pyrolysis temperature of biochar production significantly decreased its decomposition rate (Fig. 2). For example, biochar produced at 200–375 °C decomposed faster than that pyrolyzed above 375 °C. Nonetheless, based on the available dataset involving ^{13}C and ^{14}C studies, no significant difference between biochar groups produced at higher temperatures was obtained (except that produced at 1200 °C). The decomposition rate decreases with increasing pyrolysis temperature because of the increased portion
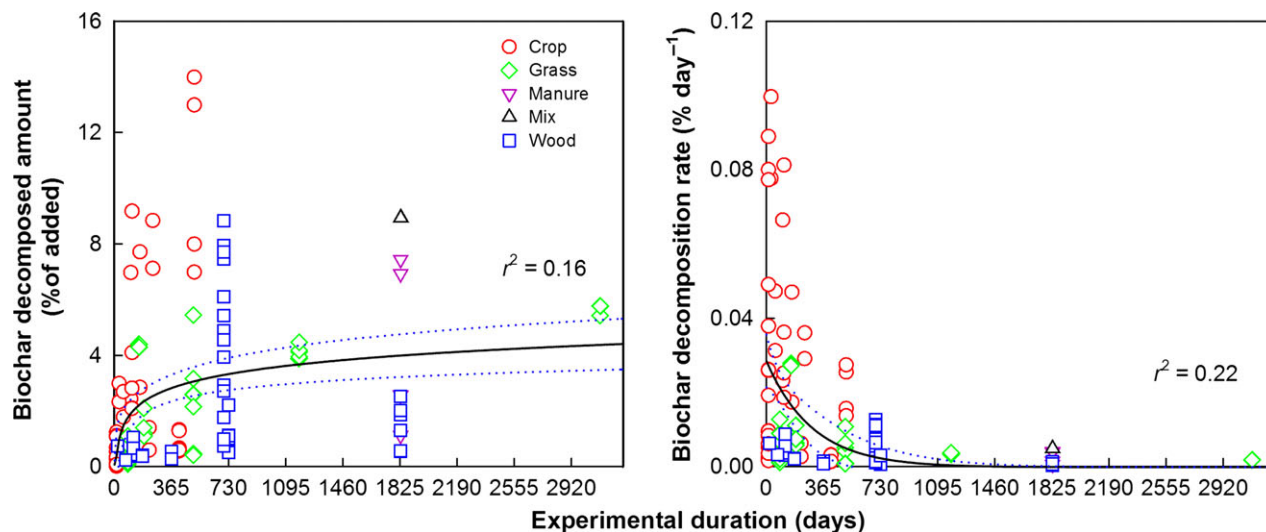

Fig. 1 Relationships between the decomposed amount (% of added, left) and rates of biochar (% day^{-1}, right) and experimental duration (days). Data are grouped based on biochar feedstocks. The dotted line indicates the 95% confidence band.
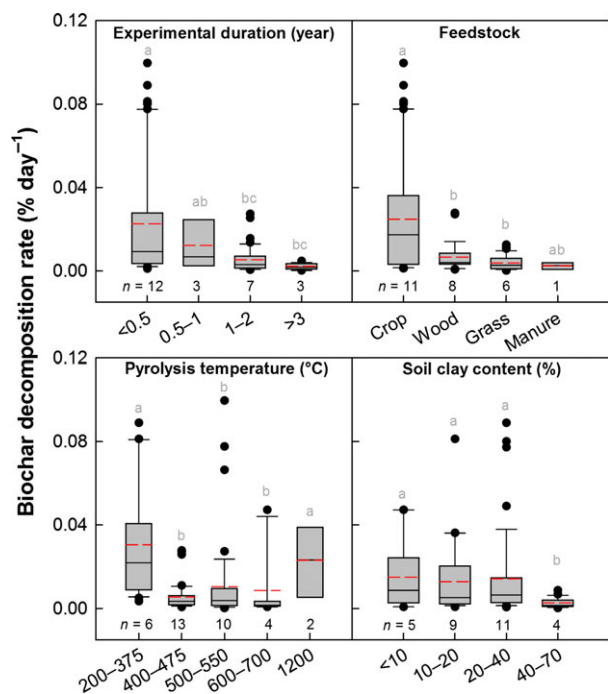
Fig. 2 Comparisons of biochar decomposition rates among different groups of the significant explanatory variables based on Table 1. Within each panel, significant difference among groups is indicated by different lower case letters (Kruskal–Wallis ANOVA, $P < 0.05$). The black solid and red dashed lines, lower and upper edges, bars and black circles represent the median and mean values, 25th and 75th, 10th and 90th percentiles, and outliers of all data, respectively. Number of studies included from each group is inserted next to x-axis.

of aromatic C and the higher degree of aromatic condensation in biochar as confirmed previously (Singh et al., 2012b; Crombie et al., 2013).

A slower decomposition rate of biochar was common in soils with the highest clay content (mean: 0.003% day^{-1}, 40–70%), whereas no significant difference was found among soils with lower clay content (Fig. 2). Moreover, aged biochar mineralized at similar rates in a chronosequence of high-biochar-containing anthrosols with various clay contents ranging from 9% to 36% (Liang et al., 2008).

The MRT varied greatly among studies, ranging from less than three up to 891 years, with an average of 107 years. Similar to other organic materials added into soils, biochar decomposition can be approximated well by biphasic patterns. The commonly used double first-order exponential decay model yielded rates for labile and recalcitrant biochar pools of 0.0093% day^{-1} and 0.0018% year^{-1}, respectively. This corresponds to MRTs of 108 days and 556 years, respectively (Fig. 3; Table 2). The labile and recalcitrant pools represent 3% and 97% of biochar C, respectively, which are close to the results

of the longest study (Kuzyakov et al., 2014). The calculated MRTs for both C pools of biochar are much shorter than previously assumed in both soils (Schmidt et al., 2002; Singh et al., 2012a) and ocean sediments (Masiello & Druffel, 1998). This is because most of the results in the database are derived from incubation studies (Table S1), the durations of which are much shorter than the MRTs of biochar. The optimal conditions and short-term duration of the experiment led to faster decomposition rates (1) than those under nonoptimal field conditions and (2) that were obtained mainly for labile C pool of biochar. Because the number of available studies is limited, there were no significant differences in biochar decomposition rate between laboratory incubations and field results (Table 1). Consequently, the available field observations do not support the standpoint that biochar can persist in soils for several thousands of years. Furthermore, current analyses of forest soils in northern Europe and Russian steppes also indicated a centennial-scale turnover of biochar (Hammes et al., 2008; Ohlson et al., 2009). Serious caution is therefore needed when extrapolating results of biochar decomposition from incubation studies to real field conditions. Despite the estimated shorter MRTs for both biochar C pools than previous findings, nearly all studies demonstrate that all biochar types are much more refractory than their precursors and natural SOM (e.g., Bruun et al., 2008; Maestrini et al., 2014a; Yin et al., 2014).

Biochar-induced priming effect

The second dataset was used for the meta-analysis to evaluate the response of biochar-induced priming effect on SOM decomposition. Averaged across all studies, biochar addition induced a negative priming effect, but this effect was not statistically significant (overall mean = −3.8%, 95% CI = −8.1–0.8%; Fig. 4). This result disagrees with the overview of Maestrini et al. (2014b), who reported a 15% increase of native SOM mineralization following biochar addition. This contradiction may primarily reflect the double number of studies in our

Table 2 Kinetic parameters of the double first-order exponential decay model describing biochar decomposition in soils. Values represent means ± standard errors

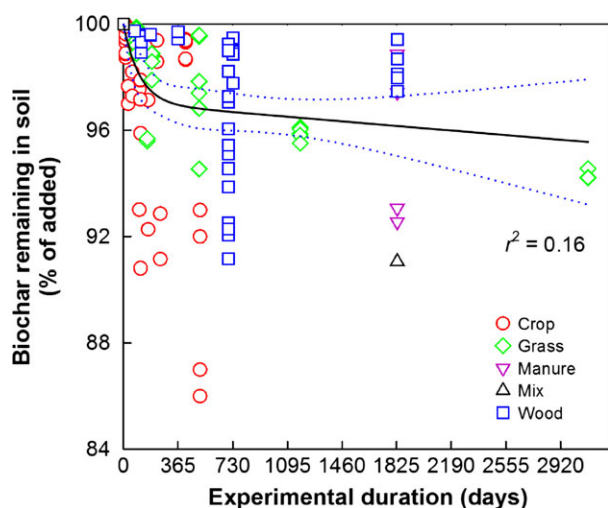|	Size	Decomposition rate	Mean residence time
Labile C pool	3 ± 0.6%	0.0093% day^{-1}	108 ± 196 days
Recalcitrant C pool	97 ± 0.6%	0.0018% year^{-1}	556 ± 483 years

Fig. 3 The percent of biochar remaining in soil plotted against experimental duration. Line represents fit of double first-order exponential decay model to the experimental data. The dotted line indicates the 95% confidence band.

Fig. 4 Comparisons of percent change of priming effects response to biochar addition among different groups of the explanatory variables of experimental duration, feedstock, pyrolysis type and temperature, application amount, and ash content of biochar, and soil clay content. Means and 95% CI are given. Number of studies included from each group is given in parentheses on the left y-axis.

database, which included 116 observations from 21 studies. Moreover, both positive and negative priming effects can coexist, whereby the latter acts over the longer term (Maestrini *et al.*, 2014b).

The biochar-induced priming effects on SOM mineralization depend on various factors including the experimental duration, the biochar characteristics, and soil properties. Except for the type and duration of experiment, along with land use, the between-group heterogeneity (chi-square test) for the remaining categorical variables was significant for the biochar-induced priming effect (Table 1). Approximately half of the studies shorter than 0.5 year showed a significantly negative priming effect (−8.6%) following biochar addition, whereas no significant effect was found in studies longer than 0.5 year (Fig. 4). Preferential substrate utilization of easily available C in biochar by soil microorganisms is responsible for the significant negative priming effect (Blagodatskaya & Kuzyakov, 2008). This is also supported by the fastest decomposition rate of biochar in those studies shorter than 0.5 year (Fig. 2). Hence, we conclude that the priming after biochar addition is induced by its easily available pools. Considering the common very high application rates of biochar (Fig. 4; Jeffery *et al.*, 2011), even a small available pool (*ca.* 3%; Table 2) is sufficient to be the source for preferential substrate utilization.

The direction and magnitude of the priming effect triggered by biochar addition varied strongly with the feedstock of biochar: The crop-derived biochar addition induced the highest negative priming (−20.3%) compared to other feedst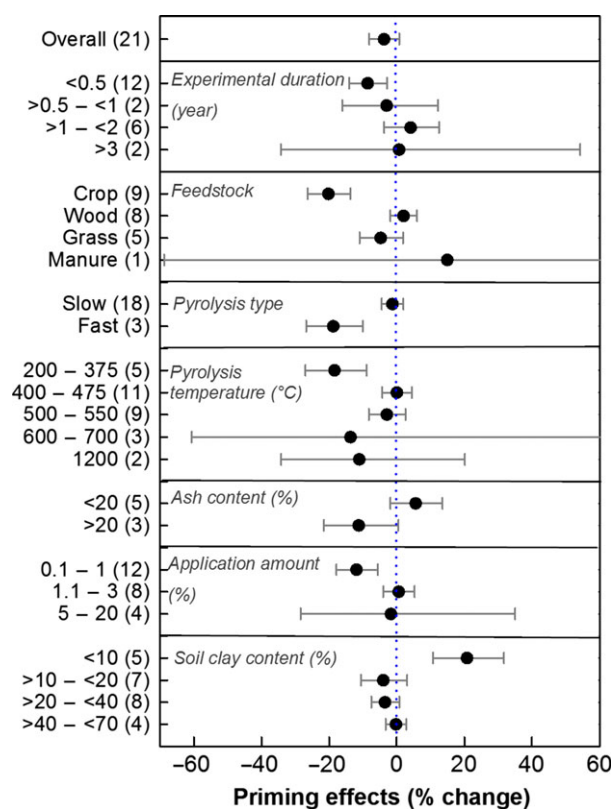ocks. As demonstrated earlier, these results are due to the higher degradability of biochar C produced from crop compared to other sources, especially wood (Fig. 2). Biochar produced either by fast pyrolysis or at the lowest pyrolysis temperature (200–375 °C), as well as a small application amount (0.1–1%), induced significant negative priming compared to other groups for each categorical variable. More bioavailable C present in biochar may result from either fast pyrolysis or lower pyrolysis temperature (Spokas *et al.*, 2011; Bruun *et al.*, 2012). Different ash contents in biochar resulted in contrasting priming effects, but this difference was insignificant. In contrast to most studies with positive priming, biochar applied to sandy soils (clay content < 10%) led to a significantly and strongly positive priming effect (20.8%). This indicates that biochar stimulates microbial activities especially in soils with low fertility.

We conclude that priming induced by biochar addition is slightly negative because of the preferential utilization of easily available substrates from incomplete pyrolysis. Although this portion is small (*ca.* 3%;

Table 2), very high biochar application rates are sufficient to trigger microorganisms to switch and thereby decreasing native SOM decomposition. Other potential reasons, for example, the presence of certain toxic compounds (phenolic nature) in biochar, may be responsible for negative priming and need to be clarified in further studies. For all studies, we definitely conclude that biochar application has a positive C balance at least within 10 years (Kuzyakov *et al.*, 2014). This means that adding biochar to soil increases the C content even by positive priming in some soils.

Factors and processes affecting biochar stability

Biochar and soil properties. The overwhelming evidence suggests that biochar is very slow decomposed in soils. Understanding the factors affecting its degradation is thus critical to maximize the long-term C sequestration potential and for soil fertility improvements in the context of changing climate and intensified land use. The intrinsic biochemical recalcitrance of biochar is primarily determined by the feedstocks and pyrolysis conditions (Fig. 5, left). Biochar produced from residues of crops and grasses is generally more degradable than that from wood, which is probably attributed to inert properties of various feedstocks, such as the high lignin content (Bird *et al.*, 1999). Pyrolysis temperature significantly affects the proportion of nonaromatic and aromatic C, as well as the degree of condensation of aromatic C in biochar (Preston & Schmidt, 2006). The

molar ratio of oxygen to carbon (O:C) is a function of pyrolysis temperature, making the O:C ratio positively correlated with biochar degradation (Spokas, 2010; Crombie *et al.*, 2013; Cross & Sohi, 2013). Current studies have proposed that biochar, as one of the not mineral-associated SOM components, is persistent in soils, perhaps reflecting the high aromaticity of biochar C (Marschner *et al.*, 2008). Supporting this, glycolipids, phospholipids, and neutral lipids (and probably carbohydrates) were the major constitutes of biochar decomposed over 3.5 years of incubation, whereas the condensed aromatics (BPCA) remained nearly unaffected during this period (Kuzyakov *et al.*, 2014). Hence, the pyrolysis temperature is critical for the C sequestration potential of biochar.

The initial quality of the SOM also affects biochar degradation (Fig. 5, left). In SOC-poor soils, labile biochar compounds deliver substrate for microorganisms within the first few months to years. For SOC-rich soils, however, biochar can stimulate SOM mineralization (Cross & Sohi, 2011; Stewart *et al.*, 2013). Biochar strongly sorbs organics in soils, especially low molecular weight organics, which then become unavailable for microorganisms (Zimmerman *et al.*, 2011; Maestrini *et al.*, 2014b). At the same time, the sorption of organics can block both the enzymes from accessing the biochar surface as well as oxidation and dissolution of biochar components (Kasozi *et al.*, 2010; Bailey *et al.*, 2011). Hence, biochar degradation depends on the soil characteristics, but the details of these interactions still require
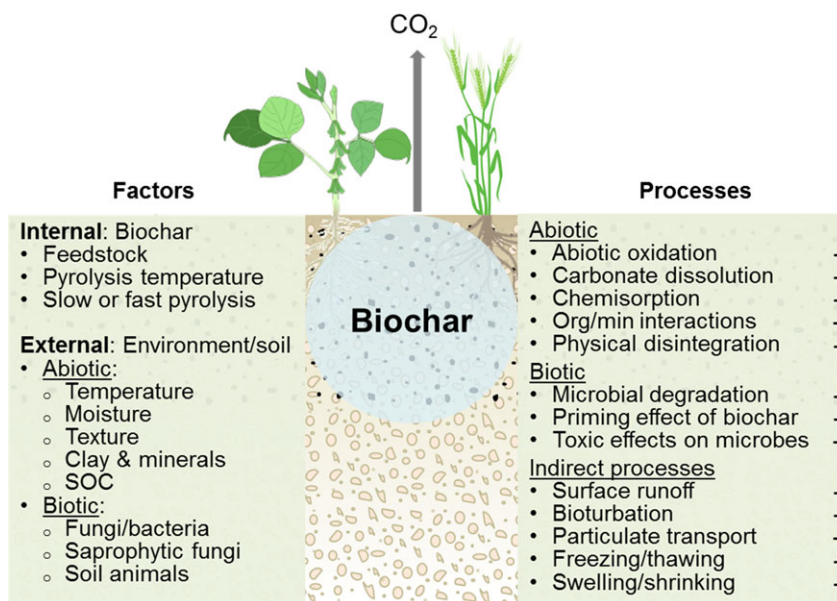

Fig. 5 Overview of factors and processes affecting biochar decomposition in soil. Internal (biochar) and external (environment/soil) factors are included (left). Abiotic, biotic and indirect processes are presented (right). The plus (+) and minus (−) signs indicate the positive and negative effects of different processes on biochar decomposition. See text for further explanation.

specific mechanistic investigations. Repeated addition of glucose or plant residues strongly stimulates biochar degradation (Hamer *et al.*, 2004; Kuzyakov *et al.*, 2009; Keith *et al.*, 2011). The accelerated decomposition is ascribed to co-metabolism (Fig. 5, right; Kuzyakov *et al.*, 2009) and continues over short periods of weeks to 2–3 months. Although we recognize the stimulated degradation due to other C input (priming on biochar), our current understanding of the effects of living plants and rhizodeposition on biochar decomposition is limited (Whitman *et al.*, 2014). As biochar decomposition is stimulated by a continuous release of rhizodeposits, future studies on the mechanisms of biochar priming in soil-plant systems are required.

Abiotic factors and processes. Biochar is characterized by high hydrophobicity (corresponding to the insolubility of its compounds) and therefore affects soil hydrophobicity (Schmidt, 2004; Knicker, 2011). The hydrophobicity contributes to aggregate formation and consequently to the spatial inaccessibility of biochar particles and other compounds (Fig. 5, right). Surface runoff has been considered as the largest biochar flux in a sandy Oxisol over 2 years, especially during the intense rain season (Major *et al.*, 2010). Very weak biochar bounding on clay minerals and its light nature could lead to preferential surface erosion on slopes compared to other organics (Rumpel *et al.*, 2006).

Biochar stability in soils may also be connected with spatial inaccessibility (physical protection) and organo-mineral interactions, particularly during the later decomposition phase (Fig. 5, right; Glaser *et al.*, 2000; Lützow *et al.*, 2006). Examining the distribution of black carbon in soils revealed that the greatest and smallest concentrations of black carbon occurred in the < 53 μm and >2 mm fractions, respectively (Brodowski *et al.*, 2006). Consequently, physical inclusion, particularly within microaggregates, at least partly contributes to the long MRTs of soil-inherent black carbon. The most biochar was recovered in particulate organic matter during the early incubation period, and this portion decreased over time (Hilscher & Knicker, 2011; Herath *et al.*, 2014). Supporting of these findings, after 10 months in a temperate forest, 74%, 20%, and 6% of biochar C were recovered in the free light fraction, aggregate-occluded, and mineral-associated fractions, respectively (Singh *et al.*, 2014). A fast association of biochar with the mineral fraction was found, but this portion decreased with time (Hilscher & Knicker, 2011). The formation of organo-mineral complexes is attributed to partial biochar oxidation, which provides negative surface charges of initially hydrophobic material (Glaser *et al.*, 2000; Hilscher & Knicker, 2011). Nevertheless, more studies are necessary to prove con-

tradictory results of organo-mineral interactions on biochar stability in soils (Glaser *et al.*, 2000; Marschner *et al.*, 2008).

Previous studies confirm that abiotic processes such as carbonate dissolution and chemisorption play an important role in biochar degradation (Fig. 5, right; Cheng *et al.*, 2006; Zimmerman, 2010; Jones *et al.*, 2011). For example, the CO_2 released from incubations under abiotic conditions (sterilized sand and nutrient solution) amounted to more than half that of microbially inoculated incubations over a one-year period (Zimmerman, 2010). Nonetheless, such results remain to be proven in rigorous experiments because nearly all transformation processes in soils are driven by microorganisms (Kuzyakov & Blagodatskaya, 2015). In an artificial weathering approach, physical disintegration is suggested to pronouncedly contribute to the considerable biochar loss, although the values varied greatly with the feedstock and pyrolysis temperature (Spokas *et al.*, 2014). Abiotic oxidation and physical disintegration can facilitate the subsequent microbial metabolization of highly aromatic biochar, such as by forming smaller particles and further increasing microbial accessibility.

Very few studies conducted at temperatures above 30 °C concluded that biochar degradation is accelerated with increasing incubation temperature (Fig. 5, left; Nguyen *et al.*, 2010; Zimmermann *et al.*, 2012; Fang *et al.*, 2014a,b). Oxidation is the most important decomposition mechanism, mainly through increases in O and hydrogen (H) contents, decrease of C content, and formation of O-containing functional groups (−COOH, =C=O, −OH), providing surface negative charges. Comparing biochar mineralization in the field during different periods (e.g., 1 vs. 11 years), the relative contributions of biotic and abiotic factors to biochar-derived CO_2 might be modified by temperature, but depends on the biochar age (Zimmermann *et al.*, 2012). Furthermore, biochar decomposition is controlled by site-specific climatic conditions, particularly temperature (Preston & Schmidt, 2006). Analyzing the historical black carbon samples along a climosequence revealed a strongly positive relationship between black carbon oxidation and mean annual temperature (Cheng *et al.*, 2008). Finally, the temperature sensitivity of SOC mineralization of biochar-amended soils may decrease with increasing incubation temperature (Nguyen *et al.*, 2010; Fang *et al.*, 2014a).

Moisture plays an important role in biochar degradation (Fig. 5, left). A modeling study of biochar movement in soil indicates that biochar mineralization was quite sensitive to variation in moisture (Foereid *et al.*, 2011). Biochar degradation was strongly increased under unsaturated and alternating saturated–unsaturated conditions compared to saturated conditions (Nguyen &

Lehmann, 2009). These authors argued that enhanced biochar mineralization was attributed to the increase in carboxylic and −OH functional groups under unsaturated and alternating conditions. Oxygen depletion contributes to the increased MRT of biochar in waterlogged ecosystems such as sediments and paddy soils (Knicker, 2011). For example, the formation of a high content of aromatic and carboxyl C in ancient Chinese paddies is attributed to the cultivation mode of paddies involving fire under drying–rewetting alternation conditions (Cao et al., 2006; Hu et al., 2009).

Biotic processes. Despite certain abiotic processes, biochar decomposition in soils is primarily microbially mediated (Fig. 5, right). Solid-state ^{13}C NMR spectroscopy showed alteration of biochar, including the formation of O-containing functional groups and the loss of aryl C structures; this was attributed to biotic oxidation and degradation (Hilscher et al., 2009). Increasing evidence suggests microbial degradation of biochar in soil. After 3.5 years of incubation, biochar-derived C in microbial biomass ranged between 0.3% and 0.95% of the ^{14}C input, whereby these proportions gradually decreased over time (Kuzyakov et al., 2014). Nonetheless, we assume that this ^{14}C incorporation was mainly connected with microbial utilization of incompletely pyrolyzed products. More specifically, the utilization of biochar C is also confirmed through its incorporation into microbial PLFA structure (Santos et al., 2012; Farrell et al., 2013). Gram-positive bacteria are known to be significant consumers of aromatic and recalcitrant compounds, and they are confirmed to be responsible for the early utilization of biochar C (Santos et al., 2012; Farrell et al., 2013). This confirms that the incorporation of biochar C into microorganisms mainly involves the labile organics still present after pyrolysis. At the later incubation period, the incorporation of biochar C into the fungal PLFAs became dominant over bacterial PLFAs (Farrell et al., 2013). In addition, the differently promoted growth of some microbial groups may be connected with the feedstocks of biochar (Steinbeiss et al., 2009). Despite due to the lack of available data about saprophytic decomposition of biochar, there is evidence that biochar can be decomposed by saprophytic fungi (Wiednera & Glaser, 2013).

The biotic mechanisms of biochar degradation remain unclear. Considering the high molecular weight of biochar, its nonregular aromatic structure, hydrophobicity and insolubility, we expect that either exoenzymes or fungi hyphae may affect initial degradation. Oxidative exoenzymes, such as peroxidases, phenol oxidases, and laccases, are commonly responsible for degradation of polyphenolic compounds such as lignins, tannins, and suberins (Baldrian, 2006; Blagodatskaya & Kuzyakov,
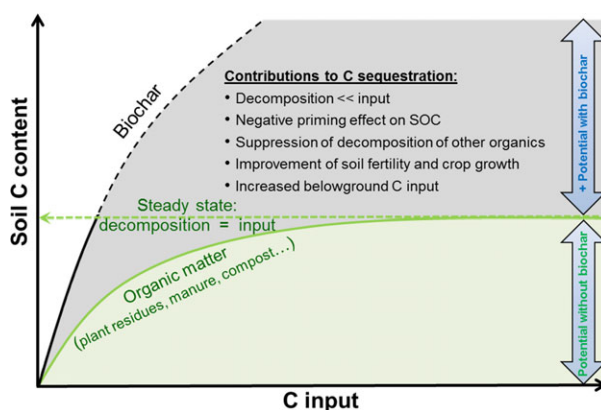

Fig. 6 Schematics for potential contributions of biochar addition to soil C sequestration. The solid and dashed green lines indicate the equilibrium and steady state of C in soils after organic matter input, respectively. The black line indicates the possible curve of C equilibrium following biochar addition. Modification from Six *et al.* (2002) and Lehmann *et al.* (2006).

2008) and can thus also oxidize complex biochar molecules. Because these enzymes require abundant oxygen, biochar decomposition under anoxic conditions (e.g., flooding of paddy soils) is much slower than in well-aerated soils. Considering that fires are natural events microorganisms should have at least some adaptations for utilizing pyrogenic products. We are, however, unaware of specific enzymes released by microorganisms for decomposing pyrogenic compounds.

Indirect processes. Translocation of biochar into deeper horizons can increase its persistence in soil (Lorenz & Lal, 2014). Biochar may be moved to subsoil by bioturbation or particulate transport (Fig. 5, right; Skjernstad et al., 1999; Ameloot et al., 2013). Leifeld et al. (2007) estimated biochar migration rates of 630–1160 mm year^{-1} in peat soils, where 21–69% migrated below the incorporation depth of 0.3 m, down to a maximum of 1.14 m over 95 years. Such extreme migration rates, however, may reflect strong overestimation due to unclear sources of biochar over longer periods. After 10 months *in situ* in a temperate forest, 3–4% of the applied biochar was recovered below the application depth, suggesting very slow downward movement (Singh et al., 2014). This redistribution mainly involves bioturbation by soil animals such as earthworms. In contrast, only 0.02–0.45% of applied biochar in a sandy Oxisol moved over 2 years below 0.3 m depth as particulate organic C and DOC (Major et al., 2010). Those inconsistencies between studies assessing downward redistribution are connected with (1) uncertainties of previous source and deposition estimations of biochar, (2) intensity of bioturbation by burrowing animals, and (3) possible cracks

and pores in soil related to periodic drying/rewetting events. Last, but not the least, other indirect processes such as freezing/thawing and swelling/shrinking dynamics may significantly affect on biochar particle size (Fig. 5, right). These processes may directly contribute to the physical breakdown of biochar. Moreover, the reduced particle size of biochar would facilitate further microbial decomposition by increasing the accessible surface area.

Implications of biochar stability for C sequestration in soil

The total area burned and fire intensity around the world are projected to increase in a warming climate. This will not only increase CO_2 emission, but also promote the conversion of biomass to pyrogenic organic matter from wild and anthropogenically induced fires. Furthermore, the climate-negative C budget of biochar together with its properties for fertility improvements lead to the expectation of further increasing biochar application to agricultural soils (Glaser et al., 2002; Lehmann, 2007). Considering its acknowledged importance as a C sink, the extremely slow decomposition of biochar may have direct and indirect implications for the C sequestration potential in soils. Biochar input is the direct contribution to C sequestration in soils (Fig. 6). Our current meta-analysis shows that biochar has a very low turnover rate (overall median: 0.0046% day^{-1}). The faster turnover of the labile pool is insignificant, as this pool amounts to only 3% of the biochar C. Ninety-seven percent of the added biochar can persist in soils on a centennial scale. Therefore, its high recalcitrance plays an important role in abating climatic change directly by sequestering C from biochar input (Woolf et al., 2010). Indirect effects are based on the impacts of biochar on SOM decomposition, sorption of easily available organics, and higher C input by plants into the soil. Pooling all studies together, biochar addition clearly contributes to a negative priming. This is also partly supported by the finding of Maestrini et al. (2014b) that biochar amendment may result in a negative priming effect over long-term period. Consequently, besides directly adding recalcitrant C to soil, biochar indirectly affects C sequestration by lowering SOM decomposition rates, at least for several years after application.

Biochar application can suppress the mineralization of labile organic matter via sorption: this gradually increases C stabilization and thereby enhancing SOC stocks (Fig. 6; Liang et al., 2010; Keith et al., 2011; Maestrini et al., 2014b). Moreover, by improving soil fertility, biochar can stimulate plant growth and thereby boost the belowground biomass input by roots and rhizodeposition. Last, but not least, the beneficial effects of biochar amendment on plant production may directly stimulate more C input into soils via plant residue return and rhizodeposition (Biederman & Harpole, 2013). Biochar application also decreases soil bulk density and improves soil biotic properties (Lehmann et al., 2011). We therefore expect not only better root growth, but especially better root distribution and allocation of more C into subsoil. Overall, our review demonstrates that biochar remains in soils for a very long time and that its stability could make it a promising tool to help abate climatic change by long-term sequestering C in soils.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Table S1. Characteristics of studies included in this meta-analysis.