



REVIEW PAPER

# The role of biochars in sustainable crop production and soil resiliency

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## Abstract

Biochar is a promising soil additive for use in support of sustainable crop production. However, the high level of heterogeneity in biochar properties and the variations in soil composition present significant challenges to the successful uptake of biochar technologies in diverse agricultural soils. An improved understanding of the mechanisms that contribute to biochar–soil interactions is required to address issues related to climate change and cultivation practices. This review summarizes biochar modification approaches (physical, chemical, and biochar-based organic composites) and discusses the potential role of biochar in sustainable crop production and soil resiliency, including the degradation of soil organic matter, the improvement of soil quality, and reductions in greenhouse gas emissions. Biochar design is crucial to successful soil remediation, particularly with regard to issues arising from soil structure and composition related to crop production. Given the wide variety of feedstocks for biochar production and the resultant high surface heterogeneity, greater efforts are required to optimize biochar surface functionality and porosity through appropriate modifications. The design and establishment of these approaches and methods are essential for the future utilization of biochar as an effective soil additive to promote sustainable crop production.

**Keywords:** Biochar, carbon sequestration, greenhouse gas mitigation, modification, surface property, sustainable crop production.

## Introduction

Currently, climate change has become one of the most serious global problems and greatly threatens our earth. Increasing global warming in particular brings a series of negative effects to agricultural development, including drought, extreme weather disasters, and soil degradation (Piao *et al.*, 2010; Chauhan *et al.*, 2014; Lesk *et al.*, 2016). On the other hand, agricultural soil is an important source of non-CO<sub>2</sub> greenhouse gas

emission (N<sub>2</sub>O and CH<sub>4</sub>) because huge amounts of fertilizer are being used to increase crop yield to sustain the increasing world population, particularly for developing countries. For example, ~47% and 58% of total anthropogenic emissions of CH<sub>4</sub> and N<sub>2</sub>O, respectively, are estimated to have resulted from the agriculture sector in 2005 (Smith *et al.*, 2007). Simultaneously, high intensities of land use and fertilizer employment can also

Abbreviations: CEC, cation exchange capacity; HM, heavy metal; HTT, heat treatment temperature; nSOC, native soil organic carbon; nZVI, nanoscale zero-valent iron; SOC, soil organic carbon; WHC, water-holding capacity.

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lead to other environmental problems, such as soil acidification (Guo *et al.*, 2010), water pollution (Zhu and Chen, 2002; Le *et al.*, 2010), and soil organic carbon (SOC) degeneration. Therefore, the development of sustainable crop production to counter the adverse impacts of global warming, while also improving soil quality and reducing greenhouse gas emission, is very important.

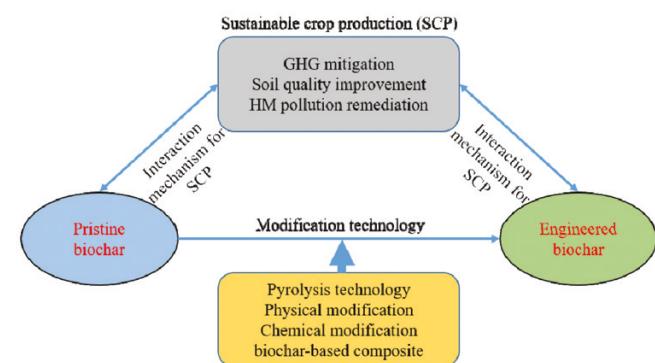
Biochar is a C-rich material that can be produced from a wide range of organic feedstock, including wood, crop residues, animal manure, sewage sludge, and other organic waste (Zhao *et al.*, 2013; Luo *et al.*, 2015; Lian and Xing, 2017) by different methods under oxygen-limited conditions, including traditional charcoal production, slow/fast/microwave pyrolysis, gasification, hydrothermal carbonization, and flash carbonization (Meyer *et al.*, 2011; Mašek *et al.*, 2013; Oo *et al.*, 2018). A considerable number of studies have demonstrated that biochar application can greatly enhance the soil quality, such as the soil physical structure and water-holding capacity (WHC) (Burrell *et al.*, 2016), SOC content (Luo *et al.*, 2016), and nutrient retention capacity (Peng *et al.*, 2011). Meanwhile, the high content of recalcitrant C in biochar is beneficial for C sequestration and for reducing greenhouse gas emission from the soil (Zimmerman, 2010; Singh *et al.*, 2012; Sui *et al.*, 2016; Han *et al.*, 2018; Borchard *et al.*, 2019). Furthermore, biochar can also immobilize heavy metal (HM) and reduce its bioavailability to the crop due to its high sorption affinity for HM (Bian *et al.*, 2014; Puga *et al.*, 2015; Li *et al.*, 2016; Xu *et al.*, 2016; Yin *et al.*, 2017), which is helpful in the recovery of crop productivity and reduces the potential risk to food safety from HM-contaminated soils. However, a consensus on the benefit of biochar amendment has not been reached, probably because of the heterogeneity of biochar properties (such as porosity, elemental composition, and functional groups) and complex interactions between biochar and solid components (organic matter and minerals) as well as biota in the soil. Therefore, more efforts should be made to modulate the properties of biochar or design smart biochar products to effectively contribute to the sustainable crop production in the era of climate change, which calls for a better understanding of the main environmental processes and mechanisms in the soil–biochar–biota triangular systems (Mandal *et al.*, 2016; Rajapaksha *et al.*, 2016; Li *et al.*, 2017; Wang *et al.*, 2018).

A number of reviews have systematically summarized the effects of biochar on soil nutrient utilization and greenhouse gas emission (Ding *et al.*, 2017; M. Hussain *et al.*, 2017; Nguyen *et al.*, 2017; Li *et al.*, 2018), as well as HM remediation (Mandal *et al.*, 2016; Li *et al.*, 2017). However, limited suggestions have been made regarding the design and modification of biochar as a promising soil amendment for sustainable crop production under a changing climate. Therefore, the main objectives in the present review are (i) to systematically discuss the critical role of biochar in the main aspects for sustainable crop production, including C sequestration, non-CO<sub>2</sub> greenhouse gas emission (CH<sub>4</sub> and N<sub>2</sub>O), soil quality improvement, and HM remediation; (ii) to identify the key properties of biochar that play a crucial part in the aforementioned aspects; and (iii) to summarize the current approaches for the production and modification of biochar, including the selection of feedstock

and pyrolytic condition, physical/chemical modifications, and biochar-based composite, and provide suggestions for engineering specific biochar to meet the demand of sustainable crop production. The effects of biochar on soil properties and HM removal are not included in our main text but are summarized in the Supplementary data and Supplementary Table S1 at JXB online, and the application of biochar for organic pollutant removal was also not covered because of the recent reviews by others (Lone *et al.*, 2015; Oliveira *et al.*, 2017; Tan *et al.*, 2017).

## Carbon sequestration in soils

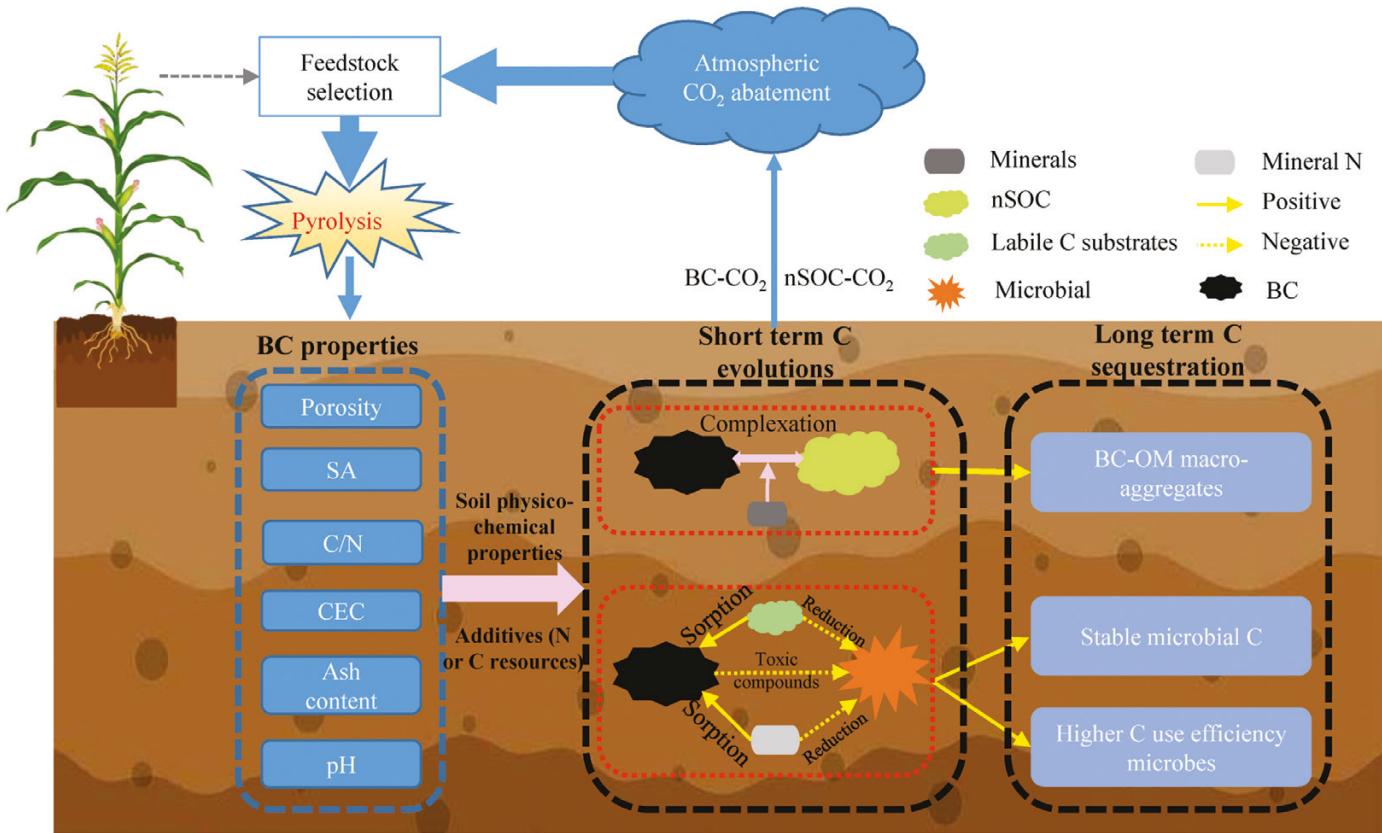
Biochar is a highly recalcitrant form of organic C in soils, and its mean residence time is estimated to be from decades to more than thousands of years (Supplementary Table S2). However, a very slow decomposition process of biochar has also been observed, which depends on the physicochemical properties of the biochar and on the ambient environment. At least two forms of C are identified in biochar, namely condensed and labile C: the former is highly recalcitrant to abiotic and biotic degradation, but the latter is relatively more degradable and would be a potential source for the emission of CO<sub>2</sub> (Nguyen *et al.*, 2010; Fang *et al.*, 2015). For example, the labile C from corn straw biochar contributed to 68.1–71.2% of the total cumulative CO<sub>2</sub> emission after being added to soil (Lu *et al.*, 2014). Therefore, the balance between the remaining biochar-C in the soil and the increased CO<sub>2</sub>-C from native SOC (nSOC) is critical for biochar's C sequestration potential in soil (Fig. 1). Thus, quantitative studies should be conducted to assess the stability of biochar in soil, as well as the direction and magnitude of biochar-induced nSOC change rather than the total CO<sub>2</sub> emission. In this section, the stability of biochar and the quantitative or structural changes in nSOC induced by biochar, which are crucial to the soil C sequestration, are discussed in detail.



## Stability of biochar in soils

### Mechanisms of biochar degradation

Although biochar is relatively stable in soils because of the high content of aromatic C, it must be degraded at some rate (Zimmerman, 2010), and the degradation rate mainly depends on the property of the biochar and the environmental conditions



**Fig. 1.** Illustrative diagram for the main processes of biogenic and native SOC-C transformation in a biochar (BC) application system. In the short term, after biochar application, soil CO<sub>2</sub> emission may be increased because of the fast release of labile C from biochar and additional nSOC degradation (co-metabolism with biochar labile C). In the long term, the soil C sequestration potential may be enhanced mainly through two aspects: (i) the formation of stable BC-organic matter macro-aggregates from the interaction between biochar and nSOC and (ii) the changes of quantity and structure of the microbial community. The dotted yellow arrows indicate the negative effects on substrate availability or microbes. The solid yellow arrows indicate the positive effects on substrate sorption or C sequestration.

(Cheng *et al.*, 2008; Nguyen and Lehmann, 2009; Spokas, 2014). Both abiotic and biotic processes are regarded as the two main processes for biochar degradation in the environment. An increasing number of studies have revealed that an abiotic process (e.g. chemical oxidation) may be the main contributor for biochar degradation in soils (Cheng *et al.*, 2006; Nguyen *et al.*, 2010), especially in the initial fast degradation phase. For example, the content of O-containing groups, O/C ratio, and cation exchange capacity (CEC) of biochar were significantly increased after incubations (Nguyen *et al.*, 2010; Rechberger *et al.*, 2019). In addition, Bruun *et al.* (2008) found that no microbial assimilation of <sup>14</sup>C-labeled biochar-C was detected after a 20 d incubation. However, some other studies have suggested that the biotic process should not be neglected and is even comparable with the abiotic process in some situations (Hamer *et al.*, 2004; Zimmerman, 2010; Farrell *et al.*, 2013). For instance, a time lag before the first sharpest increase in the CO<sub>2</sub>-C evolution (6 d after incubation) was detected in a previous study (Hamer *et al.*, 2004), which probably occurred because of the growth of microorganisms and then promoted the degradation of biochar (Hamer *et al.*, 2004). Likewise, approximately half of the biochar degradation was contributed by the biotic process, based on the comparison of 1 year abiotic and microbial incubations of different biochars (Zimmerman, 2010).

The degradation mechanism of biochar has been well examined in the literature; however, the effect of climate change on the relative importance of abiotic and biotic processes is less understood. Climate change would probably influence soil conditions (e.g. soil temperature and moisture) and composition, as well as the activity of the biota, all of which play an important role in the degradation of biochar in soils. Thus, a systematic evaluation of the stability of biochar and the design of novel biochar products are needed to increase C sequestration and reduce greenhouse gas emission in the face of climate change.

#### Key properties of biochar that contribute to its stability in soils

The stability of biochar exposed to chemical oxidation and microbial degradation is highly determined by properties such as the C morphology at both micro- and nanoscales (Nguyen *et al.*, 2010). Biochar can be more stable in soils when it has a higher degree of order and larger clusters with more side chains linked to neighboring aromatic clusters (Nguyen *et al.*, 2010). Nguyen *et al.* (2010) reported that corn biochar with lower heat treatment temperature (HTT) (350 °C) was less stable than oak biochar with higher HTT (600 °C), because the corn biochar had a less ordered structure and smaller cluster size. Additionally, Fang *et al.* (2015) found that the mean residence

times of high-temperature biochar were dramatically higher than those of the low-temperature biochar, and the stability of high-temperature biochar was less affected by soil properties than low-temperature biochar. The authors attributed this observation to the higher content of aromatic C (especially the condensed aromatic C) in high-temperature biochars (Fang *et al.*, 2015). However, notably, biochar stability is also related to the raw material used (Han *et al.*, 2018), which is even more important than HTT when considering the potential total C sequestration (Zhao *et al.*, 2013). Hence, the selection of a suitable combination of feedstock and pyrolysis conditions is essential when designing biochar with high C-sequestering capacity in soils.

In addition, the developed porous structure and large surface area can also contribute to the stability of biochar through interactions with soil minerals (Li *et al.*, 2014; Yang *et al.*, 2016; Y. Yang *et al.*, 2018) and soil organic matter (Du *et al.*, 2016; Zheng *et al.*, 2018). New metallic compounds or organometallic complexes can be formed on the biochar surface and/or in the pores, which can significantly increase the C recalcitrance index (Yang *et al.*, 2016). The C recalcitrance index was increased from 44.6% to 45.9–49.6% when walnut shell biochar was incubated with different soil minerals (FeCl<sub>3</sub>, AlCl<sub>3</sub>, CaCl<sub>2</sub>, and kaolinite) (Yang *et al.*, 2016). Furthermore, the stability of biochar also may be enhanced by the adsorption of labile C or organic matter from soils, which could form macroaggregates around biochar and protect it against microbial degradation (Du *et al.*, 2016; Zheng *et al.*, 2018).

The labile C within biochar has been suggested to be utilized by microbes in the soil and thus partially affects the degradation efficiency of biochar by microorganisms (Luo *et al.*, 2013). However, a previous study found that only 1.5–2.6% of the remaining biochar was incorporated into microbial biomass after 624 d of incubation when <sup>14</sup>C-labeled ryegrass-derived biochar-C was measured in the microbial biomass (Kuzyakov *et al.*, 2009). A similar result was also found in the study of Bruun *et al.* (2008). They concluded that biochar degradation in soils is driven mainly by co-metabolism rather than serving only as a C source for microorganisms. Changes in soil microbes (in both activity and structure) have been suggested to be closely associated with the original C structure of the biochar and, in turn, these soil microbes influence the biological degradation process of the biochar (Zhu *et al.*, 2017). However, the interaction between the biochar C structure and microbial community still needs to be further ascertained, and its effect on biochar stability also needs to be explored.

The higher content of ash/minerals in biochar may contribute to the stability of biochar in soils (Han *et al.*, 2018; Y. Yang *et al.*, 2018). Y. Yang *et al.* (2018) reported a positive relationship between the ash content and aromatic C-normalized K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>-carbon remaining values; meanwhile, these values declined after a de-ashing treatment. The authors attributed the higher stability of the original biochar to the presence of endogenous minerals within the biochars, which can protect organic matter from K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> oxidation (Y. Yang *et al.*, 2018). Co-pyrolysis with minerals has also been reported as possibly significantly increasing the aromatic C content of biochar relative to untreated biochar (Li *et al.*, 2014), and thus this process may help enhance biochar

stability. However, some other studies have suggested that the presence of ash/minerals may partly break the aromatic structure of the biochar and reduce cross-links between the layers (Nguyen and Lehmann, 2009), which would enhance the microbial activity and indirectly promote biochar biotic degradation (Nguyen and Lehmann, 2009). Thus, how the composition of endogenous ash/minerals affects the morphology and structure of biochar and its stability in soils still needs further investigation (Y. Yang *et al.*, 2018).

In summary, the mechanism of microbe-mediated biochar degradation is much less understood than that of abiotic-mediated degradation. Moreover, the studies on long-term biochar stability are much scarcer than those on short-term stability (Supplementary Table S2). Therefore, more studies are needed to investigate how the interactions between the biochar and microorganisms influence the stability of biochar over the long term. Furthermore, biochar stability can be greatly improved by the addition of biochar into mineral-rich soils (e.g. clayey soils; F. Yang *et al.*, 2018a) or by loading minerals into the feedstock or biochar (Li *et al.*, 2014; Y. Yang *et al.*, 2018). However, information on these topics is still limited. Two aspects should be further examined to demonstrate the stability of biochar and reveal the underlying mechanisms: more varieties of biochars should be tested in soils with different mineral compositions, and a greater range of mineral types being incorporated into biochar under different pyrolysis conditions (e.g. feedstock and HTT) should also be examined. Finally, current studies on the stability of biochar in soil are mainly conducted in the laboratory (such as the incubation experiments) and do not involve plants (Supplementary Table S2); therefore, knowledge about biochar decomposition in real soil environments is extremely limited.

### Native SOC stabilization

#### Mechanisms of native SOC stabilization by biochar

Positive (Wardle *et al.*, 2008; Luo *et al.*, 2011) and negative (Zheng *et al.*, 2018) priming effects or no effects (Lin *et al.*, 2015) have been observed on the mineralization of nSOC by biochar in previous studies (Supplementary Table S3). The main mechanisms for the negative priming effect are suggested as follows: (i) microbial activity is suppressed by the adsorption of organic matter or nutrient onto the biochar surface, which limits the bioavailability of nSOC to the microbes; and (ii) nSOC is protected from microbial degradation by the formation of soil macro-aggregates (Dong *et al.*, 2016; Du *et al.*, 2016; Luo *et al.*, 2016; Zheng *et al.*, 2018). The positive priming effect may also be induced by biochar through the following two mechanisms: (i) the co-metabolic effect of fast degradation of labile organic substances (e.g. dissolved organic C) in biochar, especially during the early stage of biochar application (Luo *et al.*, 2011; Farrell *et al.*, 2013; Singh and Cowie, 2014; Yu *et al.*, 2018); and (ii) the enhancement of microbial activity by supplies of new nutrient resources and favorable habitats for microbes by biochar application (He *et al.*, 2017). Therefore, the direction and magnitude of the priming effect, as well as the underlying mechanisms, are highly dependent on the properties of biochar or tested soil, as well as their interactions.

### Key factors for biochar-induced nSOC stabilization

The changes of nSOC after biochar application are closely related to the quantity and structure of the microbial community, which are influenced by biochar in direct or indirect ways (Fig. 1). Biochar with a higher surface area and CEC generally has higher adsorption capacity for labile C and minerals, thereby reducing their availability to the microbes, which may cause changes in the structure of the microbial community (Liang et al., 2010; Zheng et al., 2018). Although the microbial biomass C has been reported to increase significantly, the metabolic quotient ( $q\text{CO}_2$ ) remained at a lower level after biochar application (Liang et al., 2010; El-Mahrouky et al., 2015; Zheng et al., 2018). The authors ascribed this phenomenon to the shift of bacterial community towards lower C turnover (higher C use efficiency) bacteria taxa due to the relatively lower organic matter availability (Liang et al., 2010; El-Mahrouky et al., 2015; Zheng et al., 2018). Furthermore, biochar with a large C/N ratio generally has high aromatic C content (this means low microbial availability) and low N content. Thus, it may mean that less available C and N is released into the soil and, meanwhile, the higher C/N ratio may contribute to the adsorption of the mineral N onto biochar and thus limit the N availability (Zheng et al., 2018). A negative correlation between biochar's C/N ratio and the amount of nSOC mineralization has been reported previously (Zheng et al., 2018). In contrast, other studies have also revealed that the addition of biochar into soil may favor nSOC degradation by leading to changes in the microbial community (positive priming effect). For example, biochar could supply favorable habitats for microbes because of the high surface area and developed pore structure, and because of the released labile fractions (e.g. dissolved organic C, nutrients, and other minerals) (Maestrini et al., 2014; El-Naggar et al., 2015; Luo et al., 2016; Yu et al., 2018). Improvements in the soil pH by alkaline biochar (especially in acidic soils) (Luo et al., 2011) may also contribute to the increase in microbial activity.

Soil conditions, such as the initial pH, nSOC, and N status, temperature, and moisture content (Luo et al., 2011; Y. Fang et al., 2014; Sun et al., 2014, 2016) also greatly influence the processes of biochar-induced nSOC mineralization. The potential negative priming effect was more prevalent in soils with low mineralizable SOC (Zimmerman et al., 2011; Herath et al., 2015). Soil additives (e.g. N fertilizer, glucose, and crop straws) can also affect the biochar-induced priming effect. A greater negative priming effect was detected in a treatment with additional N than in a treatment without N (Lu and Zhang, 2015). In the early stage, the magnitude of the negative priming effect in the treatment with the addition of N was stronger than that without N addition, whereas the opposite results were found in the later stage. These findings indicate that the negative priming effect in the early stage may be induced by the decreased N bioavailability for microbes due to N adsorption, and a positive priming effect (or weakening of the negative priming effect in the early stage) in the late stage may be induced by the release of mineral N from biochar (Wang et al., 2011). Other researchers have also reported that the addition of a non-biochar C resource (glucose or crop straws) can elevate (Luo et al., 2017) or reduce (Liang et al., 2010; Keith et al.,

2011; Yousaf et al., 2017) the priming effect according to the types of additive and soil, as well as the dosage of the additives. The effect of additives on the soil microbial community may be promoted or inhibited when co-applied with the biochar because of the interactions between the biochar and additive, consequently affecting the soil property. Thus, the interactions of 'biochar–additive–microbial community' under a variety of conditions (as mentioned above) and their effects on nSOC mineralization need to be further examined, and the quantitative incorporation of biochar and additives also needs to be determined. Furthermore, long-term field tests are still lacking because the biochar–additive interactions may be changed over time.

In comparison with total microbial biomass, a change in the microbial community structure (e.g. the functional diversity) may be more important for nSOC decomposition (Blagodatskaya and Kuzyakov, 2008; Liang et al., 2010; El-Mahrouky et al., 2015; Zheng et al., 2018). Additionally, the succession of the microbial community (both quantity and structure) is substantially determined by the composition and availability of biochar and nSOC (Blagodatskaya and Kuzyakov, 2008). Hence, the evolutionary strategy of the microbial community in the soil after amendment with the biochar should be further investigated.

### Interactions between biochar and nSOC

The formation of macro-aggregates ( $>250\text{ }\mu\text{m}$ ) between biochar and soil organic matter, dissolved organic carbon, or minerals, is regarded as an important mechanism for protecting nSOC from microbial degradation, especially for long-term biochar application. The addition of biochar contributes to the formation of macro-aggregates in the soil (Du et al., 2016; Zheng et al., 2018), which can increase the stability of the nSOC. For example, the proportion of macro-aggregates in the soil was significantly increased by 49–109% after the addition of corncob biochar, and the corresponding SOC concentration in the soil was improved by 92.7–120.7% (Du et al., 2016). Dong et al., (2016) also reported a significant increase in the ratio of the SOC in the macro-aggregates to the total SOC in the soil. These data clearly demonstrate a potential negative priming effect because of the protection by biochar–organic matter macro-aggregates. The formation of biochar–organic matter macro-aggregates has been suggested to be highly related to the surface properties of biochar, such as O-containing groups, surface area, and porosity (Du et al., 2016). Thus, more effort needs to be made to design biochar surface properties to effectively increase the stability of nSOC and cope with the negative impact of climate change on C release from soils in the future.

Relative to the biochar degradation process, two distinct degradation stages (early stage and late stage) occur with nSOC, for which the biochar-induced priming effect and its mechanisms in each stage are different (Zimmerman et al., 2011; Lu and Zhang, 2015; Purakayastha et al., 2016; G. Liu et al., 2017). Generally, the positive priming effect tends to appear in the early stage, whereas the negative priming effect can be found in the late stage (Singh and Cowie, 2014; Maestrini et al., 2015). The priming effect in the early stage is

more flexible and complex due to drastic interactions in the biochar–nSOC–microbe system during this period. As labile organic substances are consumed and more stable soil aggregates are formed, the mineralization of nSOC may remain at a low rate (Purakayastha *et al.*, 2016). Furthermore, the presence of plants could also potentially influence the biochar-induced priming effect on nSOC (Weng *et al.*, 2015), but the related knowledge is extremely limited. The biochar-induced priming effect on nSOC would be more complicated when plants are considered, but the results also would be more meaningful for the successful utilization of biochar in C sequestration in soils.

## Mitigation of soil non-CO<sub>2</sub> greenhouse gas emission by biochar

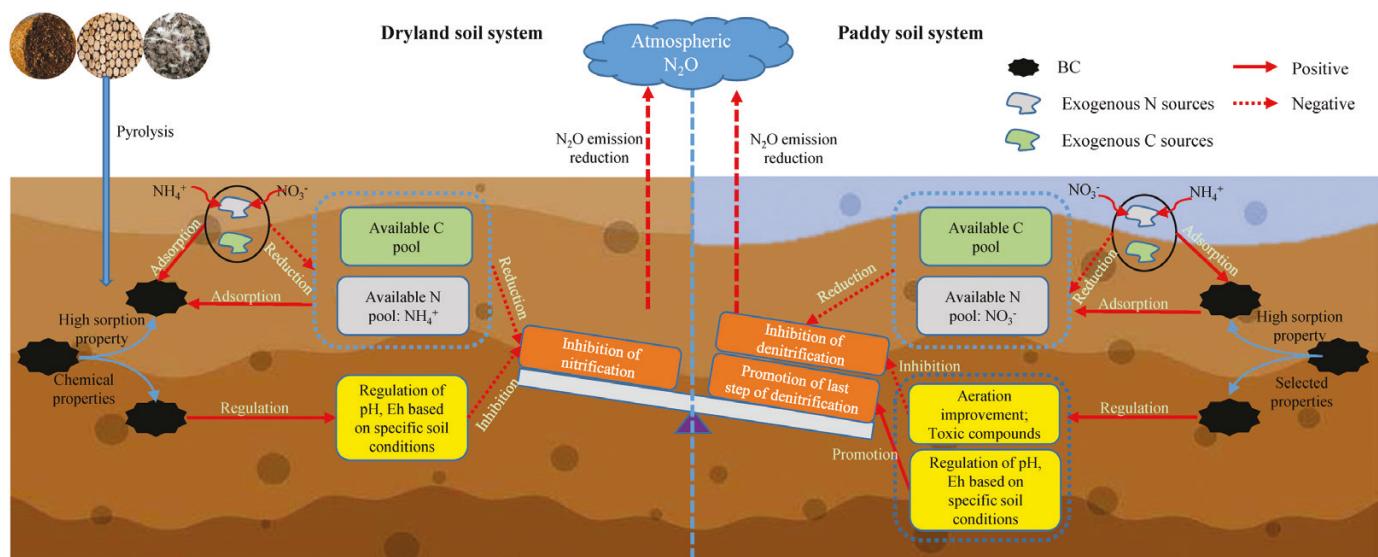
The potential reduction in emissions of CH<sub>4</sub> and N<sub>2</sub>O by the application of biochar has been widely accepted. Meanwhile, high uncertainties still exist because both the positive and negative effects of biochar on CH<sub>4</sub> or N<sub>2</sub>O mitigation have been reported frequently in previous studies (Supplementary Table S4), especially for CH<sub>4</sub> (Jeffery *et al.*, 2016; He *et al.*, 2017; Song *et al.*, 2017). The mitigation of CH<sub>4</sub> and N<sub>2</sub>O emission by biochar can be realized through various mechanisms (Figs 2, 3) and are highly dependent on the biochar properties and soil and environmental conditions, as well as the management practices.

### Key properties of biochar for non-CO<sub>2</sub> greenhouse gas mitigation

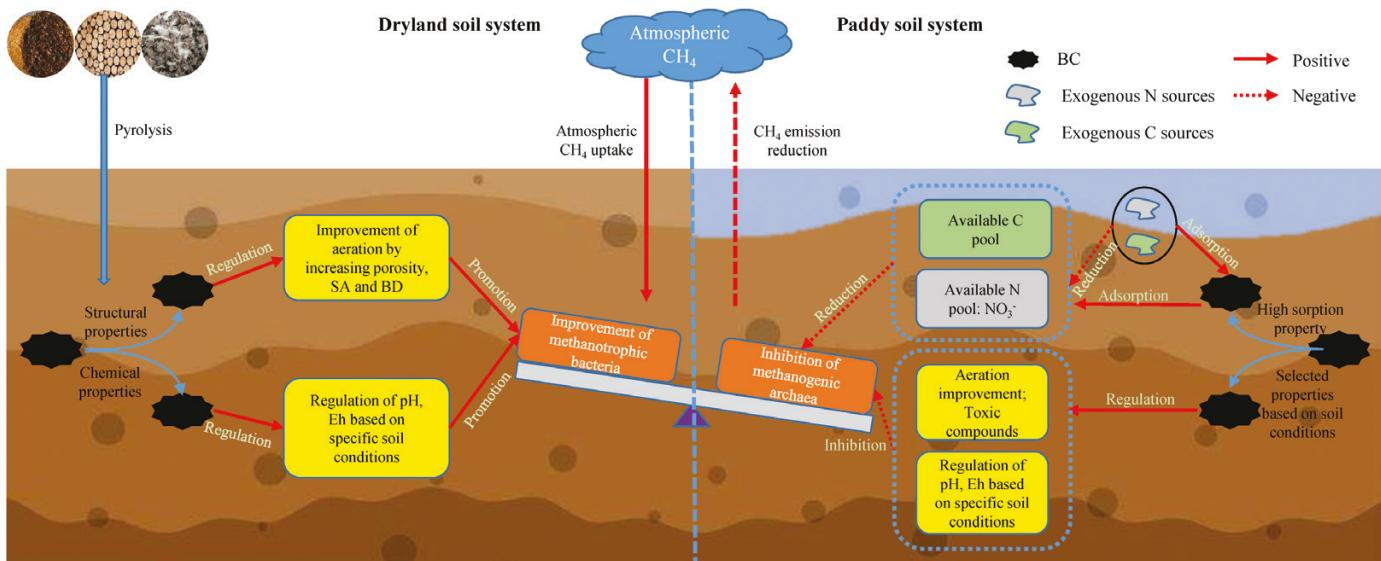
#### Physical structure: porosity and surface area

The structural properties of biochar, such as porosity and surface area, have been regarded to be among the most important properties in reducing CH<sub>4</sub> and N<sub>2</sub>O emission through

different mechanisms including the improvement of soil aeration conditions, in supplying suitable habitats for functional microbes, and in reducing the availability of C and N by adsorption (Van Zwieten *et al.*, 2009; Wang *et al.*, 2012; Wang *et al.*, 2013; Sui *et al.*, 2016; Cai *et al.*, 2018; Borchard *et al.*, 2019). Specifically, for CH<sub>4</sub>, the biochar with developed pore structure may enhance the adsorption and oxidation of CH<sub>4</sub> (Liu *et al.*, 2011; Yoo and Kang, 2012). Several studies have confirmed that the improvement of soil aeration or the supplementation of suitable habitats with biochar may be beneficial in inhibiting the activity of methanogenic archaea and/or increasing that of methanotrophic bacteria, and consequently decreasing the CH<sub>4</sub> production and/or increasing its oxidation (Van Zwieten *et al.*, 2009; Karhu *et al.*, 2011; Qin *et al.*, 2016). Fang *et al.* (2016) reported that suppressed CH<sub>4</sub> production or enhanced CH<sub>4</sub> uptake after biochar application can be achieved by increasing the soil aeration, which is helpful to the diffusion of CH<sub>4</sub> and O<sub>2</sub>. Regarding the N<sub>2</sub>O, the improvement of soil aeration by biochar application may be responsible for the reduction of N<sub>2</sub>O emission due to the suppression of the denitrification process (Ramlow and Cotrufo, 2018). However, other studies have indicated that the improvement of soil aeration may have little effect under conditions of high moisture, such as during flooding (Yu *et al.*, 2012; Lin *et al.*, 2015). Under severe water conditions (e.g. paddy cultivation system), the reduction of CH<sub>4</sub> and N<sub>2</sub>O resulting from improvement in aeration may be temporary and disappear over time due to waterlogging (Song *et al.*, 2017), and other mechanisms related to the biochar-induced changes of soil properties (e.g. pH or available substrates) may be the main contributors to the emission reduction of CH<sub>4</sub> and N<sub>2</sub>O. However, little is known about the importance of the CH<sub>4</sub> and N<sub>2</sub>O emission reduction by biochar-induced aeration improvements to the



**Fig. 2.** Schematic diagram for the potential pathways of N<sub>2</sub>O emission reduction in biochar-amended soils. In dryland soil systems, N<sub>2</sub>O emission reduction may be achieved mainly from the decrease in nitrification after biochar (BC) application, for which the available substrate reduction (e.g. C and N sources) and/or inhibition of nitrifiers are the possible mechanisms. In paddy soil systems, both the inhibition of denitrification and promotion of the last step of denitrification may contribute to the reduction of N<sub>2</sub>O emission. The dotted red arrows indicate the negative effects on substrate availability, N<sub>2</sub>O emission, or the nitrification/denitrification process, and the solid red arrows indicate the positive effects on sorption of substrates, soil property regulation, or the last step of denitrification.



**Fig. 3.** Schematic diagram of the potential pathways of  $\text{CH}_4$  emission reduction or  $\text{CH}_4$  uptake enhancement in biochar-amended soils. In dryland soil systems, the soil uptake of atmospheric  $\text{CH}_4$  may be enhanced through improving the status of methanotrophic bacteria after biochar (BC) application, for which the aeration improvement and/or soil property regulation are probably the main mechanisms. In paddy soil systems, the reduction of  $\text{CH}_4$  emission may be achieved mainly by the inhibition of methanogenic archaea after biochar application, for which the reduction of available substrates (C and N sources) and/or regulation of soil properties are the main possible mechanisms. The dotted red arrows indicate the negative effects on substrate availability,  $\text{CH}_4$  emission, or functional microbes, and the solid red arrows indicate the positive effects on atmospheric  $\text{CH}_4$  uptake, substrate sorption, soil property regulation, or methanotrophic bacteria.

total reduction of these two greenhouse gasses under the field paddy cultivation system.

Biochars with high surface area and developed porosity can also adsorb more organic or inorganic matter from the soils, such as dissolved organic C and mineral N, and thus decrease the availability of substrate resources for  $\text{CH}_4$  or  $\text{N}_2\text{O}$  production. Biochar addition has been reported to reduce  $\text{N}_2\text{O}$  emission by 50–90% by reducing the bioavailability of the C substrate to denitrifiers rather than improving soil aeration or promoting the reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  (Ameloot *et al.*, 2016). Wang *et al.* (2013) also attributed the reduced  $\text{N}_2\text{O}$  emission to the enhanced N immobilization and decreased denitrification in the biochar-amended soils. However, this mechanism may be less efficient in soils with a high content of available substrates (Angst *et al.*, 2014). Thus, the design of biochar for  $\text{CH}_4$  and  $\text{N}_2\text{O}$  reduction from soils with high substrate availability should attempt not only to enhance the surface area and porosity but also to regulate other soil properties (e.g. pH and redox potential; Chen *et al.*, 2018) based on specific soil conditions. In addition,  $\text{CH}_4$  can also be adsorbed directly by biochar, leading to the promotion of  $\text{CH}_4$  oxidation (Liu *et al.*, 2011; Yoo and Kang, 2012) and thus to a reduction in the emission of  $\text{CH}_4$ .

#### Elemental composition: H/C, C/N, available substrates, and toxic compound content

The molar H/C ratio of biochar is regarded as a key factor influencing the reduction in  $\text{N}_2\text{O}$  emission (Cayuela *et al.*, 2015; Huppi *et al.*, 2016). A positive relationship between the molar H/C ratio of biochar and the intensity of  $\text{N}_2\text{O}$  reduction has been identified, with a low molar H/C ratio (<0.3) exhibiting the highest capacity for reduction of  $\text{N}_2\text{O}$  emission

(Cayuela *et al.*, 2015). Biochar with a low molar H/C ratio generally has a higher content of condensed aromatic structures, which is more beneficial to the electron exchange between soil microorganisms and the delocalized pi-electron system on the biochar surface (Cayuela *et al.*, 2015). The role of biochar as an ‘electron shuttle’ can promote the denitrification of  $\text{N}_2\text{O}$  into  $\text{N}_2$  (Cayuela *et al.*, 2015).

The soil C/N ratio after biochar application is a key indicator for  $\text{N}_2\text{O}$  evolution (Cayuela *et al.*, 2014). Feng and Zhu (2017) found that the increased  $\text{N}_2\text{O}$  emission was negatively correlated with the TC/IN (the ratio of total C content and inorganic N content) and the nitrification was promoted when the TC/IN was <45, whereas the nitrification was suppressed when the TC/IN was >60. Similar recommendations for a C/N ratio were also reported by Vigil and Kissel (1991) where the break-even C/N ratio between the net N immobilization and mineralization of residues was 40. Therefore, the addition of biochar with high C/N may significantly increase soil C/N and suppress the emission of  $\text{N}_2\text{O}$  (Grutzmacher *et al.*, 2018). Thus, the significantly higher soil C/N in biochar treatment than that without biochar may result in greater immobilization of N instead of mineralization (Ly *et al.*, 2015). However, notably, the addition of biochar to soil with low N content may increase the emission of  $\text{N}_2\text{O}$  (Shen *et al.*, 2014). The addition of high-N biochar alone, which was generally produced from livestock manure, may significantly promote  $\text{N}_2\text{O}$  emission (Spokas and Reicosky, 2009; Yoo and Kang, 2012; Lin *et al.*, 2015; Grutzmacher *et al.*, 2018), compared with the low-N biochar produced from lignocellulosic feedstock, which exhibited little effect on the  $\text{N}_2\text{O}$  emission (Grutzmacher *et al.*, 2018) or significantly suppressed the  $\text{N}_2\text{O}$  emission (Spokas and Reicosky, 2009; Wang *et al.*, 2013). These results indicate

that the addition of N-rich biochar may also bring additional N sources into the soil for N<sub>2</sub>O production and emission.

Available substrates (e.g. dissolved organic C and mineral N) in biochar may potentially promote the emission of CH<sub>4</sub> or N<sub>2</sub>O because these substrates could help functional microbes produce both of these greenhouse gases (Singla and Inubushi, 2014; Lin *et al.*, 2015). Singla and Inubushi (2014) reported that CH<sub>4</sub> emission can be significantly increased by solid, digested, slurry-derived biochar due to the additional supply of substrates. Additionally, Korai *et al.* (2018) found that CH<sub>4</sub> emission can be reduced when biochar is extracted by hot water. However, Cai *et al.* (2018) indicated that the biochar-induced soil-dissolved organic C change may not be the dominant driving factor in CH<sub>4</sub> emission compared with other soil indicators, such as redox potential. As mentioned above, the addition of N-rich biochar is likely to promote N<sub>2</sub>O emission due to the introduction of available N substrate relative to biochar with low N content (Spokas and Reicosky, 2009; Yoo and Kang, 2012; Lin *et al.*, 2015; Grutzmacher *et al.*, 2018).

The emissions of CH<sub>4</sub> and N<sub>2</sub>O can also be reduced because of the presence of toxic compounds released from biochar (Spokas, 2013; Wang *et al.*, 2013). The capacity for soil CH<sub>4</sub> uptake was reduced in the fresh biochar treatment, whereas it was little changed in the weathered biochar treatment, which may be attributed to the elimination of toxic compounds after field aging (Spokas, 2013). Thus, polycyclic aromatic hydrocarbons in low-temperature (300–400 °C) biochar contributed to the reduced N<sub>2</sub>O emission (Wang *et al.*, 2013). However, a reduction in the N<sub>2</sub>O emission was detected in the treatments with phenolic compounds removed from low-temperature (200–400 °C) biochar (Wang *et al.*, 2013). These inconsistent results suggest that the effect of toxic compounds from biochar on the evolution of CH<sub>4</sub> or N<sub>2</sub>O needs to be further studied. Moreover, the toxic compounds in biochar may potentially affect the growth of microbes (He *et al.*, 2017), which would have profound implications for crop production.

#### Biochar pH

Soil pH is one of the most important factors that determines the composition and structure of the microbial community, for example the functional microbes related to CH<sub>4</sub> and N<sub>2</sub>O production or consumption (Feng *et al.*, 2012; Obia *et al.*, 2015). Hence, the emission of CH<sub>4</sub> or N<sub>2</sub>O can be reduced potentially through soil pH regulation by biochar. Biochar usually has a wide range of pH (4–12) (Rillig *et al.*, 2010; Schimmelpfennig *et al.*, 2014; M. Hussain *et al.*, 2017; Saenger *et al.*, 2017). Thus, the addition of biochar into soils can significantly influence the soil environment and consequently the evolution of CH<sub>4</sub> or N<sub>2</sub>O. The addition of alkaline biochar into acidic soils can significantly reduce the emission of CH<sub>4</sub> because of the improvement in soil pH (Feng *et al.*, 2012; Jeffery *et al.*, 2016). For example, CH<sub>4</sub> emission was significantly reduced by 59–63% after biochar was added to acidic paddy soil, which led to an increase in the abundance of methanotrophic bacteria because of the increased soil pH (Feng *et al.*, 2012). However, the pH effect of biochar on CH<sub>4</sub> emission was negligible in neutral soils (Jeffery *et al.*, 2016; Cai *et al.*, 2018). Therefore, the effect of biochar pH on CH<sub>4</sub> evolution relative to high-pH soils (neutral and alkaline) needs further elucidation.

In addition, increased soil pH has the potential to increase the activity of N<sub>2</sub>O reductase and thus promote the denitrification of N<sub>2</sub>O to N<sub>2</sub>, which has been reported frequently in previous studies (Yanai *et al.*, 2007; Van Zwieten *et al.*, 2009; Obia *et al.*, 2015; Tan *et al.*, 2018). Obia *et al.* (2015) confirmed that the emission of N<sub>2</sub>O can be significantly suppressed, and the emission of N<sub>2</sub> was increased when two alkaline biochars (rice husk biochar and cacao shell biochar) were added into acidic soils; the extent of N<sub>2</sub>O suppression was positively related to the alkalizing effect of the biochar. However, notably, soil pH can effectively regulate the microorganism community not only for N<sub>2</sub>O reductase but also for other denitrifiers (e.g. nitrite reductase genes, *nirK* and *nirS*) or nitrifiers that may also contribute to the emission of N<sub>2</sub>O. The role of other microorganism community changes induced by enhanced soil pH is less understood, although it is important for elucidating the mechanism of N<sub>2</sub>O emission.

#### Key soil factors affecting the performance of biochar on non-CO<sub>2</sub> greenhouse gas emission

##### Water regime/water moisture content

The moisture content (or water regime of crop cultivation, e.g. of dryland or paddy land systems) is one of the most important factors regulating the evolution of CH<sub>4</sub> or N<sub>2</sub>O (Jeffery *et al.*, 2016; Song *et al.*, 2017) because of the dominant cyclic processes of C or N in soils under different moisture conditions; thus, they will also impact on how the biochar application influences soil CH<sub>4</sub> or N<sub>2</sub>O evolution.

Meta-analysis studies have suggested that the addition of biochar to flooded soils and/or acidic soils during flooded periods as part of a management regime can significantly reduce the CH<sub>4</sub> emission (by increasing the CH<sub>4</sub> oxidation), whereas such an addition can significantly increase CH<sub>4</sub> emission (or reduce CH<sub>4</sub> uptake) in non-flooded soils (Jeffery *et al.*, 2016; Song *et al.*, 2017). However, the opposite results were also recorded in some individual studies. Rondon *et al.* (2006) reported that CH<sub>4</sub> uptake can be significantly increased after biochar addition in upland soil. Yu *et al.* (2012) found an obvious shift from CH<sub>4</sub> sink to source when biochar was added to paddy or forest soils with high water-filled pore space (100% and 85%, respectively). These inconsistent results were also recorded between the alternate water regimes of 'flooding-drainage' and completed waterlogging. The potential reduction in the CH<sub>4</sub> emission occurred in the former (Qin *et al.*, 2016; Chen *et al.*, 2018), whereas an increase in CH<sub>4</sub> emission was recorded under the completely waterlogged condition (Cai *et al.*, 2018). These results clearly demonstrate the different performances of biochar on CH<sub>4</sub> evolution under different water regimes. Generally, dryland is thought to be the sink for atmospheric CH<sub>4</sub> (Scheer *et al.*, 2011), and the capacity for CH<sub>4</sub> uptake can be promoted further after biochar application through the promotion of methanotrophic bacterial activity by the improvement of soil aeration or pH (Qin *et al.*, 2016). Under an extremely high moisture content or completely waterlogged conditions, the potential reduction of CH<sub>4</sub> emission may be mainly derived from the inhibition of methanogenic archaea activity by the reduced availability of substrate content (Lin *et al.*, 2015) or the introduction of toxic

compounds (Spokas, 2013), whereas the improvement of soil aeration may have little effect under such high moisture conditions (Yu et al., 2012; Lin et al., 2015).

The majority of reduced  $\text{N}_2\text{O}$  emission was recorded under conditions of relatively high moisture content (e.g. paddy cultivation system) with biochar addition (Q. Liu et al., 2017) (Supplementary Table S4). The reduced emission of  $\text{N}_2\text{O}$  was mainly derived from the suppressed denitrifiers (such as *nirK* and *nirS*) because of the reduced availability of N (Wang et al., 2013; Ameloot et al., 2016) or the presence of toxic compounds (Wang et al., 2013), and from the increasing reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$  by denitrification (Q. Liu et al., 2017). Under low moisture conditions (water-filled pore space <70%), nitrification was suggested as the main source of  $\text{N}_2\text{O}$  production (Sun et al., 2018; Yoo et al., 2018). For example, the source of  $\text{N}_2\text{O}$  emission coming from nitrification accounted for >80% of the total  $\text{N}_2\text{O}$  emission in most of the treatments under 60% WHC conditions (Lan et al., 2014). Q. Liu et al. (2017) indicated that  $\text{N}_2\text{O}$  emission can be significantly increased by 13% on average under low soil moisture conditions (<70% WHC), which was probably driven from the increased abundance of ammonia-oxidizing bacteria/archaea. However, the nitrification and denitrification may exist simultaneously under both highly aerated soils (Lan et al., 2014) and highly water-filled pore space soils, especially in paddy cultivation systems (Case et al., 2015; Sun et al., 2018). Sun et al. (2018) reported that the increased  $\text{N}_2\text{O}$  emission can be attributed to the enhancement of both nitrification and denitrification due to biochar application, which was confirmed by the close correlation between  $\text{N}_2\text{O}$  emission and the abundance of ammonia-oxidizing bacteria and *nirK*. Liu et al. (2014) showed that  $\text{N}_2\text{O}$  emission increased significantly (by 150–190%) within biochar treatments under the typical water regime of paddy cultivation due to the increase in the dissolvable organic C or  $\text{NH}_4^+$  in the soil.

In sum, the performance of biochar on soil  $\text{CH}_4$  and  $\text{N}_2\text{O}$  evolution can be significantly affected by the water regime employed, and the reduction mechanisms of these two greenhouse gasses are also distinct under different water regimes (Figs 2, 3). Thus, the specific properties of biochar, which are responsible for different reduction mechanisms, should be further identified correspondingly.

#### Soil pH

The evolution of  $\text{CH}_4$  or  $\text{N}_2\text{O}$  after biochar addition is significantly affected by the initial soil pH.  $\text{CH}_4$  emission reportedly can be significantly reduced in acidic soils ( $\text{pH} < 6$ ) but significantly increased in neutral soils ( $\text{pH}$  from 6 to 8) (Jeffery et al., 2016). Feng et al. (2012) found that the emission of  $\text{CH}_4$  was significantly reduced by 59–63% after the addition of biochar [produced at low (300 °C) or high (500 °C) temperature] to acidic paddy soils ( $\text{pH} 4.4$ ). In another study,  $\text{CH}_4$  emission showed greater reductions when the soil pH increased from 5.08 to 5.97–6.40 than in those soils where the pH was little changed (Shen et al., 2014). Cai et al. (2018), in contrast, reported a significant increase in  $\text{CH}_4$  when biochar was added into a neutral soil ( $\text{pH} 7.6$ ), although the soil pH was increased after the addition of biochar. Therefore, the effect of biochar on soil  $\text{CH}_4$  evolution may be dependent on the initial soil pH, which

may be affected by abundance and structure of the functional microbes under the different pH circumstances (Cai et al., 2018). For example, the initial rates of methanogenic/methanotrophic microbes in the studies of Feng et al. (2012) and Cai et al. (2018) were 0.01–0.07 and 1–4, respectively. However, Qin et al. (2016) reported that the average emission of  $\text{CH}_4$  can be significantly reduced by 17.8–9.9% because of the biochar application during a 4 year field experiment, in which the pH value (7) of tested soil was similar to that in the study of Cai et al. (2018). These inconsistent results may be attributed to the difference in the applied water regime, as discussed earlier. According to these results, we can conclude that the effect of biochar on  $\text{CH}_4$  emission through increasing soil pH is highly determined by the initial structure of methanogenic/methanotrophic microbes, which may be affected by both pH and other soil conditions.

The meta-analysis by He et al. (2017) found a negative trend between the responses of soil  $\text{N}_2\text{O}$  emission and soil pH ( $P=0.001$ ), indicating that the increased pH after biochar application may have positive potential for  $\text{N}_2\text{O}$  reduction. However, a negligible correlation was observed between the response ratios of  $\text{N}_2\text{O}$  emission and soil pH in the study by Song et al. (2017). Another meta-analysis showed that, except for acidic soil groups ( $\text{pH} < 5$ ), the addition of biochar into all pH groups exhibited a significant reduction in  $\text{N}_2\text{O}$  emission compared with the control, but little difference was detected among them (Cayuela et al., 2014). In addition,  $\text{N}_2\text{O}$  emission has also been reported as being positively correlated with soil pH, and the increased soil pH that occurs after biochar addition may significantly promote the potential denitrification rate and thus increase the  $\text{N}_2\text{O}$  emission (Liu et al., 2014). As mentioned above, soil  $\text{N}_2\text{O}$  emission can be reduced by the enhancement of denitrification (reduction of  $\text{N}_2\text{O}$  to  $\text{N}_2$ ), which is contributed by the increased soil pH after alkaline biochar application, whereas the initial abundance of denitrifier or the intensity of denitrification must be different among the soils with different pH values. Therefore, the results indicate that the change in  $\text{N}_2\text{O}$  evolution is highly dependent on the change in soil pH in biochar-amended soil.

Therefore, the soil pH-determined functional microbe abundance and microbial structure should be considered when biochar is being added to the soil to reduce  $\text{CH}_4$  and  $\text{N}_2\text{O}$  emission by regulating the soil pH. Generally, the application of alkaline biochar to acidic soils may bring about a positive reduction of  $\text{CH}_4$  and  $\text{N}_2\text{O}$ , which may not be the case for neutral or alkaline soils. Therefore, how the biochar affects the evolution of  $\text{CH}_4$  and  $\text{N}_2\text{O}$  in alkaline soils and the underlying mechanisms should be further explored.

#### Exogenous substrate application

The effect of biochar on soil  $\text{CH}_4$  or  $\text{N}_2\text{O}$  evolution can be potentially altered when labile exogenous C sources (e.g. crop straw) are added simultaneously. The addition of rice straw biochar produced at 300 °C into soil alone can significantly increase  $\text{CH}_4$  emission, whereas the  $\text{CH}_4$  emission was significantly reduced when the rice straw biochar was co-applied with rice straw (Cai et al., 2018). The increased emission of  $\text{CH}_4$  induced by the addition of labile exogenous C sources can be inhibited by biochar application (Liu et al., 2011; Cai et al., 2018). The decreased availability of dissolved organic C substrate due

to sorption to biochar may be the main mechanism for the reduction of  $\text{CH}_4$  emission (Cai *et al.*, 2018). For example, the reduced emission of  $\text{CH}_4$  was significantly related to the decreased dissolved organic C in soil, and the higher temperature biochar exhibited high reduction potential (Cai *et al.*, 2018).

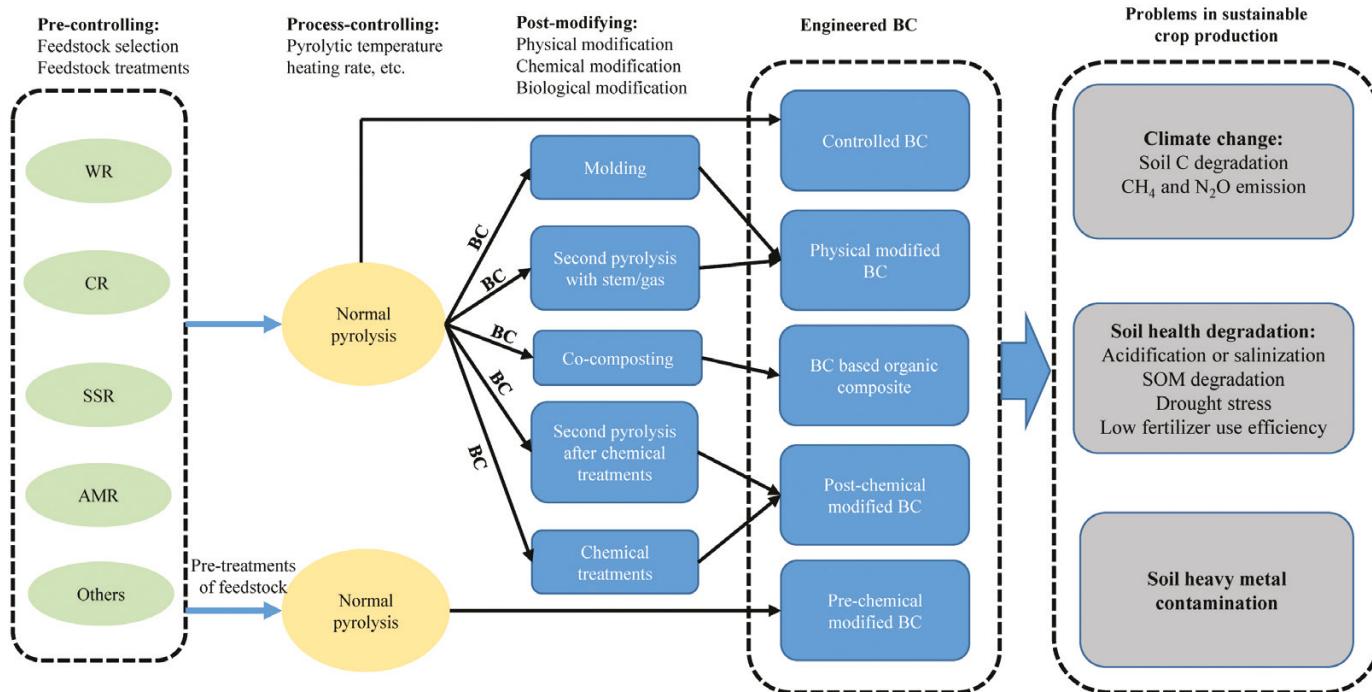
Co-application with exogenous N fertilizer can also potentially influence the  $\text{CH}_4$  or  $\text{N}_2\text{O}$  evolution in biochar-amended soils. The emission of  $\text{CH}_4$  can be significantly reduced (Hedge's  $d = -3.1$ ) in the low N application rate ( $<120 \text{ kg ha}^{-1}$ ), but that was not the case at a high N application rate ( $>120 \text{ kg ha}^{-1}$ ) (Jeffery *et al.*, 2016). Ramlow and Cotrufo (2018) reported that the increased  $\text{CH}_4$  uptake after biochar application was much greater for the treatment with no N fertilizer application than that with N fertilizer application. Furthermore, a decreased  $\text{CH}_4$  uptake rate was detected when biochar was co-applied with N fertilizer (Scheer *et al.*, 2011). The mechanism for the combined effect of biochar and N application on  $\text{CH}_4$  evolution remains unclear (Jeffery *et al.*, 2016). The variation in functional microbes in composition and structure during the interactions between biochar and exogenous N fertilizer might play an important role in  $\text{CH}_4$  evolution, which merits further investigation.

Many studies have indicated the interactive effect of biochar and exogenous N fertilizer on the  $\text{N}_2\text{O}$  emission (Wang *et al.*, 2012; Troy *et al.*, 2013; Angst *et al.*, 2014; Feng and Zhu, 2017; He *et al.*, 2017; Niu *et al.*, 2017; Grutmacher *et al.*, 2018). However, the direction and magnitude of  $\text{N}_2\text{O}$  emission as affected by this interactive effect are not always consistent. The meta-analysis showed that  $\text{N}_2\text{O}$  emission can be significantly reduced for the treatments with and without fertilizer compared with the control, and a higher reduction was recorded in the case of fertilizer use (Cayuela *et al.*, 2014; He *et al.*, 2017), which was explained by the more available N being immobilized by

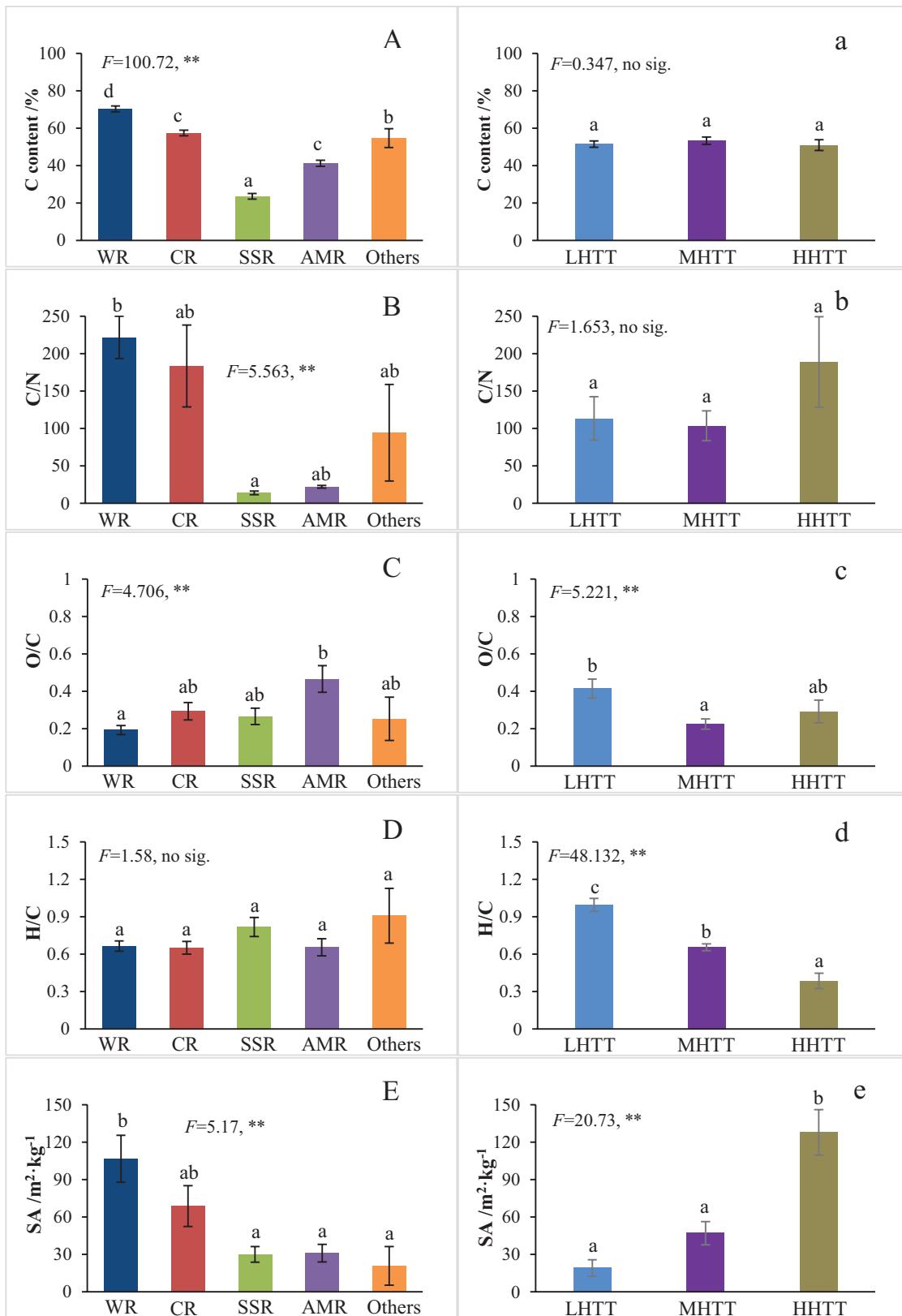
its adsorption onto the biochar. However, Chen *et al.* (2015) reported that  $\text{N}_2\text{O}$  emission was increased by 49% when biochar was co-applied with urea fertilizer at  $140 \text{ kg ha}^{-1}$  year $^{-1}$ . Troy *et al.* (2013) detected that biochar increased  $\text{N}_2\text{O}$  emission when pig manure was added jointly. In addition, little difference in the  $\text{N}_2\text{O}$  emission was found between biochar treatments and control when the livestock manure was co-utilized (providing the equivalent of  $410 \text{ kg N ha}^{-1}$ ) (Angst *et al.*, 2014). Other studies (Scheer *et al.*, 2011; B. Li *et al.*, 2015; Agegnehu *et al.*, 2016; Bass *et al.*, 2016) also recorded similar results. These data suggest that the immobilization of N by biochar adsorption may not always be the dominant mechanism regulating  $\text{N}_2\text{O}$  emission in biochar-amended soils. Different N species (e.g.  $\text{NO}_3^-$  and  $\text{NH}_4^+$ ) have distinct adsorption affinities compared with biochar, which contribute very differently to the emission of  $\text{N}_2\text{O}$  (Cayuela *et al.*, 2014; Nelissen *et al.*, 2014). Meanwhile, the additional labile C input from fertilizers would stimulate nitrifiers or denitrifiers to produce more  $\text{N}_2\text{O}$  (Troy *et al.*, 2013; Liu *et al.*, 2014). Thus, the N species and C/N ratio in exogenous N fertilizers may be important factors to consider in evaluations of their effects on  $\text{N}_2\text{O}$  emission after their application into the soil with biochar. Additionally, the interactions of biochar with different N-containing materials and aging effects should be further studied to better understand the mechanism of  $\text{N}_2\text{O}$  emission to optimize the application of exogenous N and biochar.

## Modified biochar for sustainable crop production

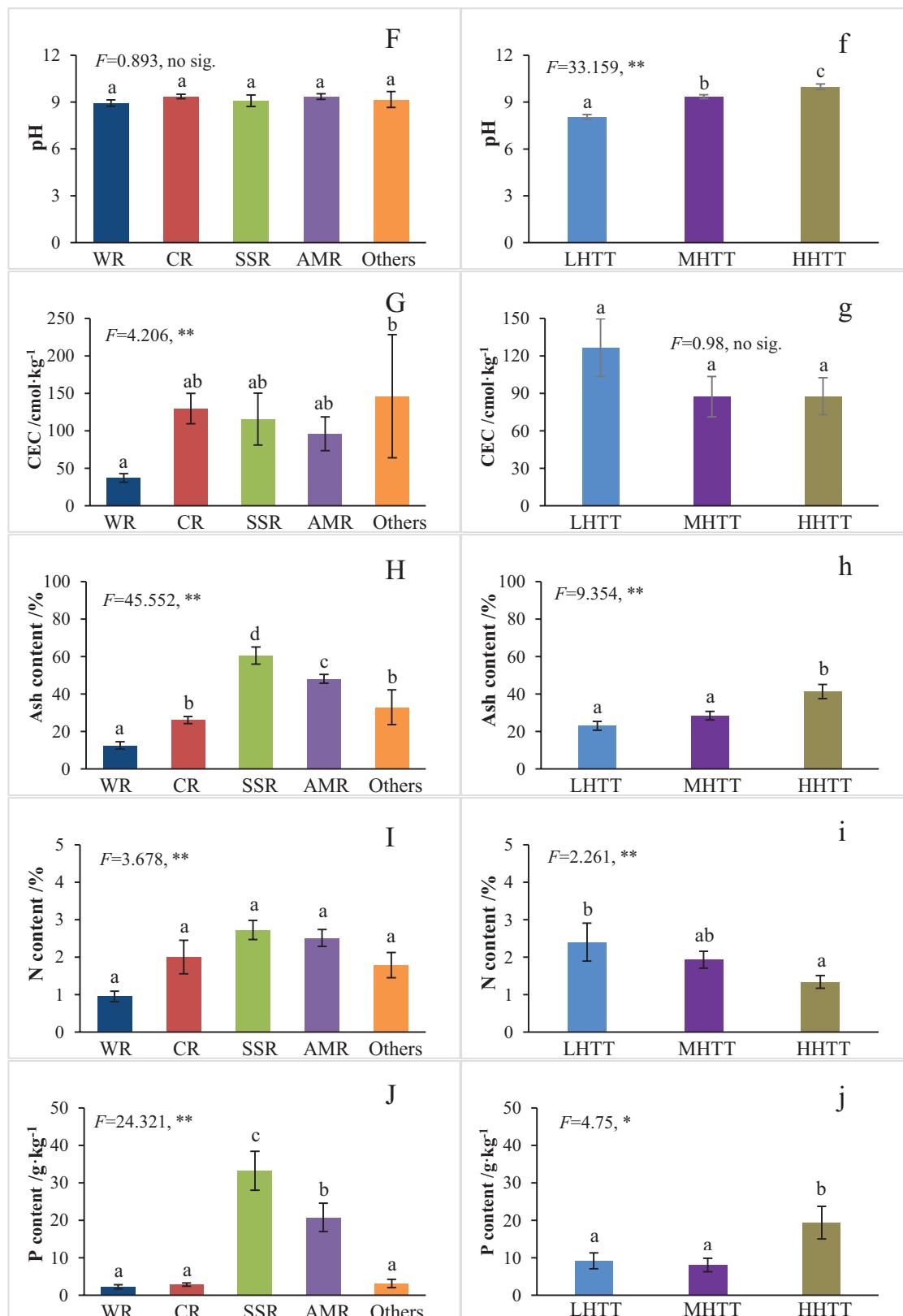
The production of engineered biochar to make it a multi-functional soil amendment for sustainable crop production has been regarded as one of the most effective approaches



**Fig. 4.** Process diagram of the engineered biochar (BC) for sustainable crop production. The abbreviations WR, CR, SSR, and AMR indicate woody resource, crop resource, sewage sludge resource, and animal manure resource, respectively.



**Fig. 5.** Effects of feedstock type and pyrolytic temperature on the selected key biochar properties. Significant differences between the groups were analyzed by one-way ANOVA with Duncan's multiple range test ( $P=0.05$ ), using Statistical Product and Service Software 25.0 (SPSS 25.0). The error bars represent the standard error, and the different letters above the error bars indicate the significant difference between them. The abbreviations WR, CR, SSR, AMR, LHTT, MHTT, and HHTT indicate woody biomass, crop residue, sewage sludge, animal manure, low heat treatment temperature ( $<400$  °C), medium heat treatment temperature (400 to 600 °C), and high heat treatment temperature ( $\geq 600$  °C).

**Fig. 5.** Continued

for its application in agriculture (Al-Wabel *et al.*, 2018). According to an overview of previous studies (Zhang *et al.*, 2016; Sizmur *et al.*, 2017; Wang *et al.*, 2018), modification methods can be classified mainly into four categories (Fig. 4): (i) the controls of general production conditions

(e.g. feedstock and pyrolytic conditions); (ii) the physical modification; (iii) the chemical modification (including pre-treatments of feedstock and post-treatments of pristine biochar); and (iv) the biochar-based organic composite (e.g. co-composting with organic waste).

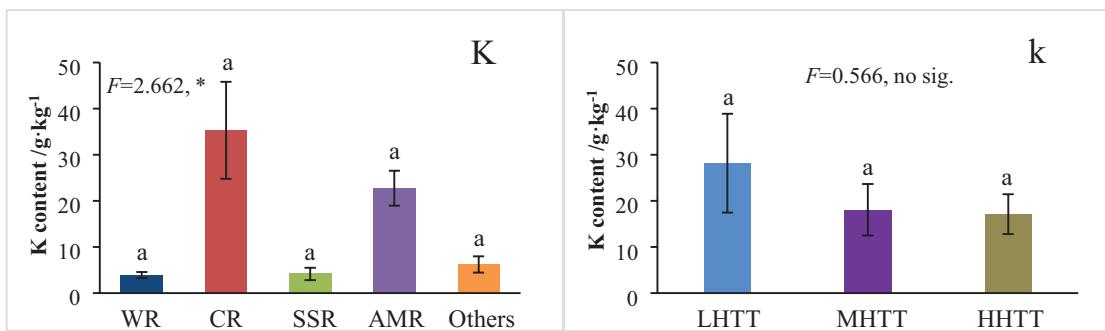


Fig. 5. Continued

### Effects of feedstock and HTT on biochar properties

Feedstock type and HTT are regarded as the most important factors for controlling biochar properties. To clarify the general roles of these two factors on key biochar properties, the relevant data compiled from previous studies (Supplementary Table S5) have been analyzed using one-way ANOVA with Duncan's multiple range test ( $P=0.05$ ). The feedstock type can greatly affect most of the selected biochar properties, except for the molar ratio of H/C and pH. The biochars produced from woody resources (WR) showed trends of higher C content, C/N, and surface area, whereas they showed lower O/C, CEC, ash content, and nutrient content (N, P, and K), than other feedstock types. In contrast, two organic waste resources, sewage sludge (SSR) and animal manure (AMR), were favorable for the production of biochars with lower C content, C/N, and surface area, and higher O/C, ash content, and nutrient content (especially for N and P). Crop resource (CR)-derived biochar fell in the middle between the WR-biochar and AMR-biochar or SSR-biochar. Relative to the feedstock type, the HTT showed a more significant impact on the molar ratios of the O/C and H/C, surface area, pH, and contents of ash, N, and P. Generally, higher HTT decreased the O/C and H/C molar ratios and the contents of the N and P, but increased the surface area and pH (Fig. 5). Overall, these results confirmed the different trends of biochar properties relative to the feedstock type and HTT (Zhao et al., 2013; Luo et al., 2015). Neither the feedstock type nor the HTT can induce a consistent trend for the changes in CEC because CEC is multi-related to cations (e.g. K, Ca, and Mg) (Zhao et al., 2013), surface area, and surface functional groups (Peng et al., 2011; Suliman et al., 2016) of biochar, and these factors vary greatly with different feedstock and/or pyrolysis conditions. Yuan et al. (2011) also reported mixed changes of CEC among the biochars produced from different feedstock and HTT. In addition, others have suggested that the nutrient properties of biochar are more greatly affected by feedstock than pyrolytic temperature (Zhao et al., 2013), which is determined by the nutrient content in the original feedstock. Thus, biochar derived from CR (higher K content) and AMR (higher N and P content) at a relatively lower temperature may be more efficient for soil nutrient improvement (Fig. 5) (Novak et al., 2009; Zhao et al., 2013).

Notably, although the biochars in the same category have a similar evolution mechanism with HTT, they can also exhibit distinct properties only because the feedstock comes from different regions. Yoo et al. (2016) reported that biochar derived

from rice straw grown in China had relatively higher N content and lower C/N than biochar from rice straw grown in Korea due to the more extensive N fertilization in China than in Korea. Therefore, we believe that differentiating biochar based on a number of key parameters of raw materials (such as C/N, mineral content and composition, or cellulose/lignin content) would be more accurate than when based just on the feedstock types.

### Physical modification

Steam/gas activation is one of the most employed physical methods used to modify biochar structure, and this method introduces an additional activation process by steam or different agent gases (e.g.  $\text{CO}_2$  or  $\text{NH}_3$ ) at high temperature after application of the traditional pyrolytic process (Rajapaksha et al., 2016; Shao et al., 2018). Generally, the surface properties, including surface area and porosity, of biochar can be significantly improved during the steam/gas activation process (Table 1) and, thereby, the adsorption capacity of biochar is enhanced. For example, after undergoing steam activation at 800 °C, the biochars derived from different materials (broiler litter, alfalfa stem, switchgrass, corn stover and cobs, guayule bagasse, and soybean straw) can exhibit significantly increased surface areas from negligible to 136–793  $\text{m}^2 \text{ g}^{-1}$ , with the corresponding volumes of the micropores reaching 0.052–0.344  $\text{cm}^3 \text{ g}^{-1}$  (Lima et al., 2010). In another study, the surface area and total pore volume were improved from  $56.91 \text{ m}^2 \text{ g}^{-1}$  and  $0.027 \text{ cm}^3 \text{ g}^{-1}$ , respectively, for unmodified corn biochar to  $755.34 \text{ m}^2 \text{ g}^{-1}$  and  $0.384 \text{ cm}^3 \text{ g}^{-1}$  for  $\text{CO}_2$  activated corn biochar (Shao et al., 2018). These increased surface areas and porosity may be attributed to the development of pore size distribution or the formation of pores and exposure of new surfaces within biochar particles by the continuous diffusion of high-temperature steam/gas into biochar particles (Lima et al., 2010; Rajapaksha et al., 2015).  $\text{NH}_3$  is another common gas used as the activating agent, which could enrich the N content and increase the N-containing functional groups on the biochar surface through ammonification (Zhang et al., 2014) (Table 1). Furthermore, the use of  $\text{CO}_2$ -ammonia mixture gas as the activation agent may result in a combination of advantages (Zhang et al., 2014). As reported by Zhang et al. (2014), the surface area, micropore volume, N content, and N-containing group could be increased when the biochar was activated by a high-temperature  $\text{CO}_2$ -ammonia mixture.

In addition to the porous structure, other properties of biochar, including pH, ash content, and element molar ratios

**Table 1.** Changes of biochar (BC) properties modified by different methods

Modification method	Modified properties	Reference
<b>Physical modification</b>		
Steam activation at 800 °C	Increases the surface area significantly: from 59.5 m <sup>2</sup> g <sup>-1</sup> to 335.1 m <sup>2</sup> g <sup>-1</sup> and from 94.2 m <sup>2</sup> g <sup>-1</sup> to 335.3 m <sup>2</sup> g <sup>-1</sup> for low and high temperature BC, respectively	Uchimiya <i>et al.</i> (2010)
Significantly increases the micropore area and micropore volume		
Steam activation at 300 °C and 700 °C	Slightly increases the pH for activated BC at low temperature, and slightly decrease it at high temperature	Rajapaksha <i>et al.</i> (2015)
Increases the ash content for both activated BCs, from 25.4% to 28.7% for low temperature and from 43.7% to 70.7% for high temperature		
Decreases the H/C, O/C, and (O+N)/C molar ratios for activated BC at low temperature, and increases these at high temperature		
Increases the surface area for both activated BCs, from 0.85 to 1.22 for low temperature and from 2.31 to 7.10 for high temperature		
Decreases the pore volume for activated BC at low temperature (from 0.004 cm <sup>3</sup> g <sup>-1</sup> to 0.003 cm <sup>3</sup> g <sup>-1</sup> ), and increases this value at high temperature (from 0.008 cm <sup>3</sup> g <sup>-1</sup> to 0.038 cm <sup>3</sup> g <sup>-1</sup> ).		
Steam activation for maize stover and wood-BC	Increases the O/C molar ratio at low pyrolytic temperature (350 °C), and decreases the O/C ratio at high pyrolytic temperature (550 °C), for both stover- and wood-BC	Fungo <i>et al.</i> (2014)
Steam activation of wood-BC	Increases the surface area after steam activation, and the maximum increase of surface area under optimum condition can reach up to 643 m <sup>2</sup> g <sup>-1</sup> in comparison with <10 m <sup>2</sup> g <sup>-1</sup> for pristine BC	Azargohar and Dalai (2008)
Steam activation of different feedstock-based BCs	Increases the surface area from negligible to 136–793 m <sup>2</sup> g <sup>-1</sup>	Lima <i>et al.</i> (2010)
CO <sub>2</sub> activation of corn-BC	Exhibits developed micropore volume, ranging from 0.052 cm <sup>3</sup> g <sup>-1</sup> to 0.344 cm <sup>3</sup> g <sup>-1</sup>	Shao <i>et al.</i> (2018)
Increases the surface area from 56.91 m <sup>2</sup> g <sup>-1</sup> (unmodified corn BC) to 755.34 m <sup>2</sup> g <sup>-1</sup>		
Increases the total pore volume from 0.027 cm <sup>3</sup> g <sup>-1</sup> (unmodified corn BC) to 0.384 cm <sup>3</sup> g <sup>-1</sup>		
Decreases the abundance of surface functional groups in comparison with unmodified corn BC		
Decreases the surface area from 56.91 m <sup>2</sup> g <sup>-1</sup> (unmodified corn BC) to 0.81–25.54 m <sup>2</sup> g <sup>-1</sup> , the extent decreasing along with increasing methanol concentration		
Decreases the total pore volume from 0.027 cm <sup>3</sup> g <sup>-1</sup> (unmodified corn BC) to 0.001–0.0194 cm <sup>3</sup> g <sup>-1</sup> , the extent decreasing along with increasing methanol concentration		
Increases the surface functional groups (especially nitrogen functional groups) in comparison with only CO <sub>2</sub> -activated corn BC, and the extent increased along with increasing methanol concentration		
Increases the atomic O/C and N/C ratios in comparison with only CO <sub>2</sub> -activated corn BC, especially at high methanol concentrations		
CO <sub>2</sub> activation for cotton stalk BC at different activation temperatures	Increases the surface area from 224 m <sup>2</sup> g <sup>-1</sup> (unmodified cotton stalk BC) to 289–556 m <sup>2</sup> g <sup>-1</sup>	Zhang <i>et al.</i> (2014)
Increase the pore volume of micropore from 0.07 (unmodified cotton stalk BC) to 0.12–0.21 cm <sup>3</sup> g <sup>-1</sup>		
NH <sub>3</sub> activation for cotton stalk BC at different activation temperatures	Increases the surface area at relatively high temperature (>600 °C) from 224 m <sup>2</sup> g <sup>-1</sup> (unmodified cotton stalk BC) to 252–435 m <sup>2</sup> g <sup>-1</sup>	Zhang <i>et al.</i> (2014)
Increases the N content at relatively low temperature <900 °C from 1.09% (unmodified cotton stalk BC) to 2.91–1.61%		
Mixed CO <sub>2</sub> –NH <sub>3</sub> gas activation for cotton stalk BC at different activation temperatures	Increases the surface area at relatively high temperature (>600 °C) from 224 m <sup>2</sup> g <sup>-1</sup> (unmodified cotton stalk BC) to 297–627 m <sup>2</sup> g <sup>-1</sup>	Zhang <i>et al.</i> (2014)
Increases the pore volume of micropore at relatively high temperature (>600 °C) from 0.07 cm <sup>3</sup> g <sup>-1</sup> (unmodified cotton stalk BC) to 0.12–0.25 cm <sup>3</sup> g <sup>-1</sup>		
Increases the N content at relatively low temperature (<900 °C) from 1.09% (unmodified cotton stalk BC) to 1.52–3.78%		
Pre-magnetic stirring orange peel powder in FeCl <sub>2</sub> and FeCl <sub>3</sub> (1:1) solution and then pyrolysis at 250–700 °C	Significantly higher content of iron oxide in modified BC than non-modified BC, and the extent increased with the increase of pyrolytic temperature	Chen <i>et al.</i> (2011)
Significantly decreases the C content, especially for MBC pyrolysis at high temperature (700 °C, only 0.424%)		
Significantly increases the H/C ratio		
Increases the ash content from 3.17–14.9% to 42.4–95.7%		
Decreases the surface area		
BC modified using microwave-synthesized magnetic iron oxide particles (FeSO <sub>4</sub> ·7H <sub>2</sub> O)	Decreases the surface area after magnetic modification for the pristine BCs with high surface area (nut shield, plum stone, and wheat straw BCs), and increases the surface area for those pristine BCs with low surface area (grape stalk and grape husk BCs)	Trakal <i>et al.</i> (2016)
Abundance of iron oxides in magnetic modified BCs		
Increases the CEC after magnetic modification for all BCs, with the exception of grape stalk BC, increases by 1.49–4.33 times		

**Table 1.** *Continued*

Modification method	Modified properties	Reference
<b>Chemical modification</b>		
Soaked BC in 0.1 M HCl solution	Decreases the pH from original 10.21 to 7.26	Guo et al. (2017)
Layered double hydroxide-modified BC	Increases the surface area from $6 \text{ m}^2 \text{ g}^{-1}$ to $30 \text{ m}^2 \text{ g}^{-1}$ for Zn/Al-MBC, $13 \text{ m}^2 \text{ g}^{-1}$ for Mg/Al-MBC, and $56 \text{ m}^2 \text{ g}^{-1}$ for Ni/Fe-MBC	F. Yang et al. (2018b)
Immersed peanut hull BC in 10% $\text{H}_2\text{O}_2$ solution for 2 h	Increases the micropore volume Decreases the pH from 6.2 (pristine BC) to 4.4 Increases the surface C oxidation of pristine BC resulting in increases of O content and O-containing functional groups Slightly increases the surface area due to the increase of surface carboxyl groups, suggesting that the $\text{H}_2\text{O}_2$ treatment could not increase the surface area dramatically through the change of pore structure of BC	Xue et al. (2012)
Immersed the BC in 10% $\text{H}_2\text{SO}_4$ solution	Minimal variation on the surface functional groups	Fan et al. (2010)
Stirred rice straw BC in KOH solution	Enhances the formation of various surface functional groups, e.g. COO-, $\text{CH}_2$ , and OH Enhances the surface area Enhances the porous structure	Bashir et al. (2018)
Immersed the wood-BC in KOH solution	Increases the surface area after KOH activation, and the maximum increase of surface area under optimum conditions can reach up to $783 \text{ m}^2 \text{ g}^{-1}$ in comparison with $<10 \text{ m}^2 \text{ g}^{-1}$ for pristine BC	Azargohar and Dalai (2008)
Stirred municipal solid waste BC in KOH solution	Increases the surface area from $29.1 \text{ m}^2 \text{ g}^{-1}$ to $49.1 \text{ m}^2 \text{ g}^{-1}$ Increases the pore volume from $0.039 \text{ cm}^3 \text{ g}^{-1}$ to $0.357 \text{ cm}^3 \text{ g}^{-1}$ Increase the O-containing functional groups	Jin et al. (2014)
Immersed BC in 10% NaOH solution	Relatively higher content of polyaromatic structure Increases the O-containing functional groups	Fan et al. (2010)
Soaked hickory BC in NaOH solution for 2 h and then heated at $600^\circ\text{C}$ for 2 h further	Slightly increases the H/C and O/C atomic ratios from 0.33 to 0.26 and 0.12 to 0.10, respectively Increases the surface area from $256 \text{ m}^2 \text{ g}^{-1}$ to $873 \text{ m}^2 \text{ g}^{-1}$ Increases the CEC from $45.7 \text{ cmol kg}^{-1}$ to $124.5 \text{ cmol kg}^{-1}$ Enhances the thermal stability Significantly increases the surface O-containing functional groups	Ding et al. (2016)
Stirred BCs in chitosan solution for 30 min and then added dropwise into NaOH solution for 12 h	Slightly increases pH Significantly decreases the surface area	Zhou et al. (2013)
Sequentially stirred BC in $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$ solutions, ammonium hydroxide solution, and with $\text{Na}_2\text{S}_2\text{O}_4$ added	Increases the H/C and O/C atomic ratios, and decreases the C/N ratio Introduces a considerable number of amino groups	Yang and Jiang (2014)
Soaked rice straw BC in $\text{FeCl}_2$ solution	Increases the total Fe content from $0.74 \text{ g kg}^{-1}$ to $35.5 \text{ g kg}^{-1}$ Decreases the pH from 10.7 to 4.87	Yin et al. (2017)
Pre-dipped ground corn material in $\text{MgCl}_2$ solution for 2 h and then pyrolysis at $300\text{--}600^\circ\text{C}$	Enriches the magnesium nanoparticles in MBC No change in surface area	C. Fang et al. (2014)
Soaked corn straw BC in $\text{KMnO}_4$ and $\text{Fe}(\text{NO}_3)_3$ solutions and further pyrolysis at $600^\circ\text{C}$ for another 0.5 h	Increases the ash content from 16.77% to 27.53% Increases the K content from $112.3 \text{ mg l}^{-1}$ to $261.4 \text{ mg l}^{-1}$ Increases the surface area from $61.0 \text{ m}^2 \text{ g}^{-1}$ to $208.0 \text{ m}^2 \text{ g}^{-1}$ Increases the $\text{pH}_{\text{pzc}}$ from 8.93 to 9.6	Lin et al. (2018)
Soaked corn straw BC in $\text{KMnO}_4$ and $\text{FeSO}_4$ solutions	Increase the ash content from 16.77% to 36.61% Increase the K content from $112.3 \text{ mg l}^{-1}$ to $259.2 \text{ mg l}^{-1}$ Decreases the surface area from $61.0$ to $7.53 \text{ m}^2 \text{ g}^{-1}$ Decreases the $\text{pH}_{\text{pzc}}$ from 8.93 to 3.17	Lin et al. (2018)
Pre-immersed feedstock in $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ solution for 2 h	Increases the ash content from 4.02% to 14% Increases the surface area more than twice Increases the pore volume more than seven times Increases the thermal stability, due to the presence of Mn-oxides	Wang et al. (2015)
Soaked pine BC in $\text{KMnO}_4$ solution with a magnetic stirrer for 2 h, and the resulting suspension was then boiled for 20 min, followed by drop wise addition of HCl solution	Increases the ash content from 4.02% to 33.4% Decreases the surface area by two-thirds Increases the pore volume by 21 times Increases the thermal stability, due the presence of Mn-oxides	Wang et al. (2015)
Pre-soaked corn cob in $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solution and stirred for 1 h, and then pyrolysis at $600^\circ\text{C}$	Increases the pH from 7.17 to 10.45 Dramatically increases the surface area from $0.07 \text{ m}^2 \text{ g}^{-1}$ to $26.56 \text{ m}^2 \text{ g}^{-1}$ Alters the surface structure and morphology	Shen et al. (2019)

**Table 1.** *Continued*

Modification method	Modified properties	Reference
Kenaf bar BC was mixed with $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and stirred for 30 min to form a mixture of the BC and iron; subsequently green tea extract was added to produce a solid and the obtained solid was separated, washed, and dried to form the designated BC–nZVI	Formation of spherical particles (with mean diameter of ~100 nm) on BC–nZVI surface Contains abundant organic functional groups including C=O, C–N, C–H and C–O.	Liu <i>et al.</i> (2018)
BC was dissolved in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and stirred for 1 h, then the $\text{NaBH}_4$ solution was added dropwise for reduction $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to nZVI	Decreases the surface area from $194.4 \text{ m}^2 \text{ g}^{-1}$ to $96.1\text{--}122.7 \text{ m}^2 \text{ g}^{-1}$ for different mass rates of BC to nZVI Decrease the pore volume from $0.98 \text{ cm}^3 \text{ g}^{-1}$ to $0.017\text{--}0.041 \text{ cm}^3 \text{ g}^{-1}$ for different mass rates of BC to nZVI Loads nZVI particle homogenously on BC surface	I. Hussain <i>et al.</i> (2017)
Wood biomass was immersed and stirred into prepared graphene oxide nanosheet (~1 $\mu\text{m}$ ) suspensions for 1 h, and then the pre-treated wood biomass was pyrolyzed in muffle furnace by slow pyrolysis at desired temperatures (300–700 °C)	Increases the BET- $\text{N}_2$ surface area from $8.38\text{--}302.8 \text{ m}^2 \text{ g}^{-1}$ to $10.97\text{--}443.9 \text{ m}^2 \text{ g}^{-1}$ ; BET- $\text{CO}_2$ surface area from $117.7\text{--}367.8 \text{ m}^2 \text{ g}^{-1}$ to $121.8\text{--}454.9 \text{ m}^2 \text{ g}^{-1}$ Significantly increases the nanoporous structure Significantly increases the active sites Significantly alters the structure of surface functional groups	Abdul <i>et al.</i> (2017)
Water hyacinth biomass was dipped into graphene oxide suspension and stirred for 1 h, followed by sonication for 2 h, and then the treated biomass was pyrolyzed in tubular furnace in $\text{N}_2$ environment at temperature of 300 °C	Introduces a sheet-like graphitic structure Increases the BET- $\text{N}_2$ surface area from $8.85 \text{ m}^2 \text{ g}^{-1}$ to $25.89 \text{ m}^2 \text{ g}^{-1}$ Decreases the pore volume from $0.025 \text{ cm}^3 \text{ g}^{-1}$ to $0.019 \text{ cm}^3 \text{ g}^{-1}$ and pore size from 1.716 nm to 1.613 nm Increases the quantity of oxygen-containing functional groups, which is indicated by the decrease of surface C/O rate from 2.93 to 2.26	Shang <i>et al.</i> (2016)
Milled hickory chips and sugarcane bagasse biomass were stirred in carbon nanotube suspensions, and then pyrolyzed in a quartz tube at 600 °C	Surface areas of hickory chips BC–carbon nanotube (1%) and sugarcane bagasse BC–carbon nanotube (1%) were ~3 and 40 times greater than pristine BCs Increases the negative charge of surface with increasing amount of carbon nanotube added Higher thermal stability for carbon nanotube-modified BCs than pristine BCs Loads the tubular carbon nanotube bundles on BC surface	Inyang <i>et al.</i> (2014)
<b>BC-based organic composite</b>		
Co-composting of BC and chicken manure	Decreases the pH from 9.7 (rice hull BC) to 8.1 Decreases the C content from 88% (rice hull BC) to 42.3% Increases the total N content from $1.3 \text{ g kg}^{-1}$ (rice hull BC) to $16.9 \text{ g kg}^{-1}$ Compared with the M treatment, BM significantly reduced soil $\text{CO}_2$ and $\text{N}_2\text{O}$ by 35% and 27%	Yuan <i>et al.</i> (2017)
Co-composting of BC and farm manure at various ratios	Increases the N content from 1.86% to 3.73–4.66%	Qayyum <i>et al.</i> (2017)
Co-composting of BC with green waste and chicken manure	Increases the nutrients from 0.24, 0.03, and 0.38% (pristine BC) to 1.15, 0.2, and 0.66% for N, P, and K, respectively Decreases the C/N ratio from 308 (pristine BC) to 30 Decreases the pH from 8.1 to 7.5	Bass <i>et al.</i> (2016)
Co-composting of BC and pig manure	Increases the pH from 7.32 (wheat straw BC) to 8.5–9.0	Zhang <i>et al.</i> , (2016)
Composted corn cob BC in rice straw	Increases the concentrations of water-soluble nutrients including $\text{PO}_4^{3-}$ , $\text{K}^+$ , and $\text{Ca}^{2+}$ Decreases the pH from 9.98 (corn cob BC) to 7.13 Increases the water-extractable organic carbon content from $1.84 \text{ g kg}^{-1}$ (corn cob BC) to $6.91 \text{ g kg}^{-1}$ Increases the CEC from $61 \text{ cmol kg}^{-1}$ (corn cob BC) to $119 \text{ cmol kg}^{-1}$ Increase the O content from 9.64% (corn cob BC) to 12.59%	Zeng <i>et al.</i> (2015)
Co-composting of BC and rice straw	Decreases the pH from 9.98 (corn cob BC) to 7.04 Increases the water-extractable organic carbon content from $1.84 \text{ g kg}^{-1}$ (corn cob BC) to $31.27 \text{ g kg}^{-1}$ Increases the CEC from $61 \text{ cmol kg}^{-1}$ (corn cob BC) to $131 \text{ cmol kg}^{-1}$ Increases the O content from 9.64% (corn cob BC) to 13.98%	Zeng <i>et al.</i> (2015)
Co-composting of BC with mill waste and sheep manure	Decreases the C/N ratio from 80.2 (BC) to 12.4 Increases the nutrients of N, P, and K from 0.84, 0.19, and 0.27% (pristine BC) to 2.69, 0.39, and 4.04%, respectively	Lopez-Cano <i>et al.</i> (2016)
Co-composting of BC with pig manure and corn stalk powder	Higher N content than BC or compost only Decreases the C/N	(R. Li <i>et al.</i> , 2015)

[H/C, O/C, and (O+N)/C], can also be changed during the stem/gas activation process. These varieties are highly dependent on the activation condition, such as the gas agent, temperature, and duration (Zhang *et al.*, 2013; Rajapaksha *et al.*, 2015). Thus, how to control the activation condition to effectively regulate the properties of biochar and their implications for soil amendment need to be thoroughly examined in the future.

### Chemical modification

The main chemical modifications for biochar include at least oxidation of acids/bases, loading of metal bases, and coating with nanoscale metal oxides or carbonaceous materials (Inyang *et al.*, 2014; Mandal *et al.*, 2016; Rajapaksha *et al.*, 2016; Abdul *et al.*, 2017; Sizmur *et al.*, 2017). Using different chemical treatments, biochar properties, including the pH, surface area, O-containing group content or species, porosity, and surface charge, can be regulated (Table 1). The general alkalinity of biochar can be reduced when biochar is treated by acidic solutions or Fe solutions. As shown in Table 1, the pH of biochars was decreased after the biochars had been soaked in solutions of HCl, H<sub>2</sub>O<sub>2</sub>, FeCl<sub>2</sub>, or Fe(NO<sub>3</sub>)<sub>3</sub> (combined with KMnO<sub>4</sub> solution). Furthermore, Shen *et al.* (2019) reported that the pH of corncob biochar increased from 7.17 to 10.45 when the corncob material was pre-treated with a MgCl<sub>2</sub>·6H<sub>2</sub>O solution. The surface area, O-containing groups, and porosity can be improved by acidic and/or base oxidation, such as H<sub>2</sub>O<sub>2</sub>, KOH, or NaOH treatments (Table 1). The changes in biochar pore size distribution and pore structure deformation were regarded as the main contributors to the increased surface area (Jin *et al.*, 2014). In addition, the CEC increased 172% when hickory biochar was soaked in NaOH solution for 2 h and further heated at 600 °C for another 2 h (Ding *et al.*, 2016).

Recently, the use of nanoscale metal oxides (e.g. oxides of Mn, Mg, and Zn), nanoscale zero-valent iron (nZVI), or carbonaceous materials (e.g. carbon-nanotube and graphene oxide nanosheet) to produce biochar-based nanocomposites was suggested as a promising pathway for synthesizing the highly efficient adsorbent for pollutant removal (Tan *et al.*, 2016). Generally, the surface area, pore properties, and functional groups can be positively improved after the biochar is coated with nanometal oxides (Table 1). However, C. Fang *et al.* (2014) reported little change in the surface area of biochar when the corn material was pre-dipped in an MgCl<sub>2</sub> solution, although the magnesium nanoparticles were enriched in the modified biochar. Even in the study of Lin *et al.* (2018), the authors found that the surface area was significantly decreased from 61 m<sup>2</sup> g<sup>-1</sup> to 7.53 m<sup>2</sup> g<sup>-1</sup> when corn straw biochar was treated by KMnO<sub>4</sub> solution. Wang *et al.* (2015) also detected a dramatic decrease in the surface area for birnessite-modified biochar, although the pore volume was 22 times greater than that of pristine biochar. Thus, the changes in biochar properties should be further examined regarding different metal oxides, biochars, and methods of incorporation.

Biochar with a large surface area and pore structure is regarded as an efficient and low-cost supporting material for nZVI stabilization (Dong *et al.*, 2017). Although the surface

properties (e.g. surface area and pore volume) may be decreased for biochar-based nZVI composites compared with pristine biochar (Table 1), the introduction of nZVI particles generally leads to a positive surface charge and high performance in reduction and catalysis (I. Hussain *et al.*, 2017; Liu *et al.*, 2018). Therefore, the biochar–nZVI composites manifested much higher pollutant removal efficiency than the biochar alone or nZVI alone, especially for the oxyanion-related HMs and organic pollutants (Bakshi *et al.*, 2018; Liu *et al.*, 2018; Lyu *et al.*, 2018). The high reducibility of the biochar–nZVI composites was suggested to be the key mechanism for HM removal (Lyu *et al.*, 2017; Bakshi *et al.*, 2018; Liu *et al.*, 2018). For example, Bakshi *et al.* (2018) revealed that As<sup>5+</sup> can be removed effectively through its reduction to As<sup>3+</sup>, coupling with the successive oxidation of Fe<sup>0</sup> to Fe<sup>2+</sup>/Fe<sup>3+</sup>, and then co-precipitation of the As<sup>3+</sup> and Fe<sup>3+</sup> to form various Fe(As)OOH phases. The catalysis/activation of biochar–nZVI composites is the main contributor to degradation of the organic pollutant (I. Hussain *et al.*, 2017; Liu *et al.*, 2018), I. Hussain *et al.* (2017) reported that the biochar–nZVI can effectively enhance the degradation of nonylphenol (optimal removal rate reached up to 96.2% within 120 min) by activating the persulfate to generate sulfate radicals. In one of the more recent studies, Dai *et al.* (2019) found that a 2D biochar–ZVI composite, synthesized from lignocellulosic waste (old corrugated containers) and FeCl<sub>3</sub>·H<sub>2</sub>O, exhibited high efficiency toward bisphenol A degradation by activating either peroxyomonosulfate or H<sub>2</sub>O<sub>2</sub>. The authors ascribed this high catalytic activity of 2D biochar–ZVI composite to the synergistic effect of the Fe<sup>0</sup> species, the ketonic C=O groups, and the intrinsic graphene oxide-like 2D structure (Dai *et al.*, 2019). Consistent results were also recorded by Liu *et al.* (2018). Additionally, coating with nanoscale carbonaceous materials (e.g. graphene or carbon nanotube) could also effectively enhance the adsorptive performance of biochar-based composites (Inyang *et al.*, 2015; Shang *et al.*, 2016; Tang *et al.*, 2016; Abdul *et al.*, 2017). The surface area, nanoporous structure, and potential active sites can be dramatically increased for biochar-based graphene/carbon nanotube composites, due to the loading of new nanostructures, such as a sheet-like graphitic structure and tubular carbon nanotube bundles (Inyang *et al.*, 2014; Shang *et al.*, 2016; Abdul *et al.*, 2017). Therefore, biochar-based nanocomposites can be an effective method for specific pollutant removal/degradation. However, the stability and efficiency of these new promising biochar-based nanocomposites should be further examined extensively, in which the roles of the synthetic method or mixture proportion (nanomaterial to biochar), as well as the components and properties of nanomaterial and pristine biochar, should be considered (Dong *et al.*, 2017; I. Hussain *et al.*, 2017).

To summarize, the aforementioned results indicate that the surface functionality of biochar can be designed for specific applications. However, the composition heterogeneity of the feedstock inevitably leads to the distinct surface properties of biochar as mentioned above, although the same chemical modification/material is carried out under strictly controlled conditions. Among the heterogeneous features, the presence of inorganic species may be one of the most important factors, which greatly affects the reactions during the modification.

Thus, how to effectively control the negative impact of these inorganic species in the chemical modification and/or utilize them as natural activators should be examined in future studies on the design of biochar and biochar-based products. Additionally, the biochar-based nanocomposites may be a promising method to produce an efficient functional biochar; however, studies regarding this aspect remain limited. Finally, the physicochemical stability of modified biochar, especially those loaded with metals, nanoparticles, or biochar-based nanocomposites, in the soil matrix is relatively less well examined, which would be an important criterion for evaluating the performance of biochar products in real applications.

#### *Biochar-based organic composite*

Co-composting biochar with organic waste not only can accelerate the composting process but can also improve the quality of the ultimate compost product due to the interactions between biochar and organic waste as well as with the micro-organisms. During the composting process, the properties of added biochar, such as the surface functional groups, CEC, pH, and nutrient retention, can also be altered accordingly. Thus, adding biochar into the organic compost process made the added biochar itself and biochar-based organic composite exhibit apparent improvement in comparison with biochar or organic compost without biochar (Table 1). For example, *Zeng et al.* (2015) reported that the pH of corn cob biochar was reduced from 9.98 to 7.13, whereas the water-extractable organic carbon content, CEC, and O content were significantly increased after composting. For the biochar-based composite, lower pH and C/N, and higher O content, CEC, and nutrient (N/P/K) retention were observed relative to the compost without biochar (Table 1). Furthermore, the stability of the biochar-based organic composite can also be enhanced, although the organic matter degradation may be increased during composting (*Dias et al.*, 2010; *Zhang et al.*, 2016). *Dias et al.* (2010) found an extremely high humic acid fraction in the alkali-extractable fraction (>90%), which indicated the high intensity of the humification of the biochar-based organic composite. This alteration may be very favorable to improvements in the structure and quantity of soil organic matter when the biochar-based organic composites are applied to the soils.

In summary, most previous studies of biochar modification or biochar-based organic composite, especially the physical and chemical modifications, were aimed at improving the properties of biochar related to its sorption capacity of HMs and organic compounds in water and soil environments. However, the modified biochars or biochar-based composites, which are characterized by high surface area and porosity, enriched nutrient or mineral content, and/or abundance of surface functional groups, may also provide other benefits in soil improvement, such as increasing the SOC stability, mitigating greenhouse gas emission, and enhancing soil quality. Unfortunately, these aspects are less well examined in the literature. Moreover, the production cost will inevitably increase because of additional production processes or input of chemical materials, especially for physical and chemical methods. Owing to the large demand for biochar for soil improvement,

the economic feasibility of modified biochar or biochar-based composite application in crop production systems should be assessed. Comparatively, the biochar-based organic composite may have more integrated benefits (e.g. better organic waste management and nutrient recycling) for environment and crop production than the physical and chemical modifications. However, challenges still exist to more precisely control the properties of biochar-based organic composite due to the complicated biochar–microbe–organic material interactions under variable composting conditions. Thus, more studies should be conducted to investigate how to design better biochar-based organic composites for more effective applications in sustainable crop production.

#### **Conclusions and future perspectives**

In this review, the potential benefits of biochar in carbon sequestration, reduction of greenhouse gas emission, soil quality improvement, and HM remediation are discussed in detail (for detailed discussion of the latter two aspects, see the Supplementary data). Based on the analysis of the relationship between biochar properties and functions, the key composition and structure of biochar that play a crucial role in the above-mentioned aspects are also recognized. Finally, the current engineered modifications of biochar for sustainable crop production have been reviewed. Although biochar shows great potential in the promotion of sustainable crop production, many knowledge gaps still exist. Specifically, five aspects of research that need to be addressed are outlined as follows.

- (i) The relationship between biochar properties and its benefit for crop production/environment should be explored comprehensively in a full variety of biochar/soil/environment conditions, based on which the key biochar properties with respect to specific purposes should be identified. This is the critical foundation for guiding the future of engineered biochar practices.
- (ii) Direct and indirect interactions between biochar and microorganisms play a critical role in the functions of biochar on crop production and environment. However, the relationships between biochar properties and microbial community succession have not been thoroughly illuminated. Thus, the interactions between biochar properties and functional microbial communities under different scenarios (different soil/environmental conditions or specific soil/environmental issues) should be examined systematically.
- (iii) A large portion of current studies on modified biochar are mainly related to its sorption capacity for contaminants in water and soil systems. Information on the performance and related mechanisms of the influence of these modified biochar on other aspects (e.g. soil property and greenhouse gas emission) when they are applied to soils is still extremely limited.
- (iv) Along with increasing the variety of engineered biochar, investigations are needed into the optimal modification technical routes under a wide range of soil/environmental conditions regarding performance

efficiency, environmental impact, and economics of each engineered biochar. Furthermore, the differences between engineered biochars and other amendments should also be discussed. Thus, methods, such as life cycle assessment and the analysis of cost-benefit or cost-effectiveness, are needed to quantitatively assess these aspects in both modeling and empirical ways.

(v) The production of biochar and its use are involved in a complicated system with multiple stakeholders (e.g. producer, user, and policymaker) (Oliveira et al., 2017). Thus, effective collaboration that can link all the stakeholders together to promote the development of biochar technology for better agricultural and environmental utilization needs to be addressed and developed.

## Supplementary data

Supplementary data are available at *JXB* online.

S1. Benefits of biochar for soil health.

S2. Remediation of heavy metal (HM) pollution.

Fig. S1. Links of key biochar (BC) properties and mechanisms for heavy metal (HM) immobilization.

Table S1. Summary of the responses of soil HM bioavailability, HM uptake by plants, and the crop productivity to biochars (BC) added to HM-contaminated soils.

Table S2. Biochar (BC) stability test by the soil mineralization experiments.

Table S3. Summary of soil C responses to biochar (BC) application.

Table S4. Summary of the responses of  $\text{N}_2\text{O}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$  emissions in various soils to the applications of biochar (BC) produced under different conditions.

Table S5. Original studies used for the compilation of the biochar property data set.

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