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REVIEW

Exploring long-term effects of biochar on mitigating methane emissions from paddy soil: a review

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Abstract

Biochar has been reported to mitigate short-term methane (CH_4) emissions from paddy soil. Currently, CH_4 mitigation by biochar has primarily focused on the abundance and variations of methanogens and methanotrophs, and changes in their activities during methane production and consumption. However, long-term effects of biochar on methane mitigation from paddy soil remain controversial. This review overviewed the existing mechanisms for CH_4 mitigation as a result of biochar application. In addition, the two existing opinions on the long-term CH_4 mitigation effect upon biochar application were highlighted. Combining the already explored mechanisms of fresh biochar on CH_4 mitigation from paddy soil and a novel discovery, the potential mechanisms of biochar on long-term methane emission response were proposed. This review also revealed the uncertain responses of biochar on long-term CH_4 mitigation. Therefore, to achieve carbon neutral goal, it is important to further explore the mechanisms of long-term CH_4 mitigation under biochar application.

Keywords Biochar · Methane mitigation · Methanogens · Methanotrophs

1 Introduction

Global warming (GW) is the rise in the average earth surface temperature as a result of increase in the concentration of greenhouse gases (GHGs) including methane (CH_4), nitrous oxide (N_2O), water vapor, ozone (O_3), chlorofluorocarbons (CFCs) and carbon dioxide (CO_2) (Al-Ghussain 2019). Basically, it is the greenhouse effect that made the earth a suitable place to live. Without GHGs, there would be no life on earth because the surface temperature would be too low to live on (Anderson et al. 2016). However, the exponential increase in the concentration of GHGs in the atmosphere results in the catastrophic phenomenon, which is termed as GW. Among the GHGs, CH_4 is one of the most widespread greenhouse gases emitted from wetlands, paddy fields, coal mines, ruminants and anthropogenic activities including livestock raising and leakage from natural gas systems (Waqas et al. 2020). Methane was expected to contribute GW around 18% over next 50 years after 1999 (Milich 1999). Whereas, GW contribution of CH_4 emissions over 27% worldwide in 2015 (Ma et al. 2019). In the recent years, it has been noticed that CH_4 emission from wetlands has significantly increased to about 164 Tg year^{-1} (Bridgham 2013; Singh 2017). The total occupied earth's surface by wetlands accounts to about 3.8%, with the total global CH_4 emissions of 20–40% (Tiwari et al. 2020). Among the wetlands, paddy fields are considered as a significant contributor of CH_4 emission (Xiao et al. 2018). In the flooded paddy soils, CH_4 is produced by a group of bacteria termed as methanogens. The flooded paddy soils, such as rice fields, restrict the oxygen (O_2) supply to the soil and produce anaerobic conditions that result in the fermentation of soil organic matter and release CH_4 to the atmosphere. The release of CH_4 from deeper layer of flooded soil to the atmosphere is carried out by ebullition, diffusion, and through aerenchyma conduits of paddy plant (Singh 2017). The recent report by Food and Agriculture Organization Corporate Statistical Database (FAOSTAT) demonstrated that among the agricultural soil all around the world, the rice cultivation contributed up to 20% of the global CH_4 emissions by the end of year of 2018

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(FAOSTAT 2020). Hence, it is imperative to reduce methane emissions from paddy fields.

Biochar has been well reported as a promising material for mitigating GHGs especially for CH_4 emissions from paddy soil (Awad et al. 2018; Han et al. 2016; Wu et al. 2019a). Biochar is a black-colored carbon (C) rich material produced as a result of thermal decomposition of biomass under O_2 deficient conditions (Mia et al. 2017a; Waqas et al. 2018). The potential of biochar has been extensively explored due to its benefits in mitigation of CH_4 emissions (Nan et al. 2020b; Pratiwi and Shinogi 2016; Yoo et al. 2016). Ji et al. (2020) reported significant reduction of CH_4 emissions using biochar during an incubation experiment conducted for 77 days. In addition, the low rate (2.8 t ha^{-1}) application of biochar on paddy fields has also been reported to reduce CH_4 emissions by 41% for the short-term application (Nan et al. 2020a, b). Furthermore, a meta-analysis on biochar also revealed that the soil with application of various types of biochar significantly reduce CH_4 emissions (Awad et al. 2018). These results suggest that the ecological benefit of biochar application on CH_4 emission has been widely demonstrated.

The potential of biochar to mitigate CH_4 emission from paddy soil has been well reported in the pot experiments and short-term field studies. In contrast, the observations from long-term field effects, especially after years of biochar aging, are seldom reported. Hence, most of the mechanisms for CH_4 mitigation are limited to the application of fresh biochar. The mechanisms developed by fresh biochar on mitigation of CH_4 emissions from paddy soil mainly focus on the impacts on soil physicochemical structure and microbial dynamics. The reductions in CH_4 emission as a result of biochar addition are mainly attributed to lowering the ratio of methanogens/methanotrophs (*mcr*A/*pmo*A) (Table 1). In addition to the substantial reduction in the ratio of methanogens/methanotrophs, the other specified mechanisms are either significantly decreased activities of methanogens (Dong et al. 2013; Han et al. 2016) or substantially increased activity changes of methanotrophs (Han et al. 2016; Nan et al. 2020a; Wu et al. 2019a; Yang et al. 2013). On the other side, few studies also demonstrated the potential of biochar to mitigate CH_4 emission after years of aging process; however, their results are in controversy with similar studies (Nan et al. 2020a; Wang et al. 2019c; Wu et al. 2019a) and the exact mechanisms are still blurred. Due to lacking the long-term continuous CH_4 emission observation under biochar application in paddy fields, it is difficult to evaluate CH_4 mitigating effect of biochar amendment scientifically and realistically over decades scale. Hence, the efficacy and the mechanism of biochar in mitigating CH_4 emissions after years of aging in paddy fileds remain to be explored.

The present review offers a comprehensive overview to fully understand the long-term effects of biochar amendment and the potential mechanisms in reducing CH_4 emissions

Table 1 Mechanism of biochar on methane mitigation from paddy soil

Feedstocks	Temperature (°C)	Experiment type	Experiment duration (year)	Effectiveness duration (year)	Mechanism	References
Wheat straw	450	Incubation	–		Decreased methanogens and increased methanotrophs	He et al. (2020)
Rice straw	500	Incubation	–		Decreased methanogens	Ji et al. (2020)
Wheat straw	~500	Incubation	–		Increased methanotrophs	Wu et al. (2019b)
Rice straw	~500	Incubation	–		Decreased methanogens	(Cai et al. 2018)
Rice straw	500	Pot	1		Decreased methanogens and increased methanotrophs	Han et al. (2016)
Rape straw	500	Pot	2	2	Decreased methanogens	Qi et al. (2021)
Rice straw	–	–	–		Increased methanotrophic activity	Singh (2017)
Tobacco straw	450	Field	1		Decreased methanogens and increased methanotrophs	Huang et al. (2019)
Wheat straw	500	Field	3	2	Improved soil aeration and Eh induced enhanced methanotrophic activity	Chen et al. (2018)
Rice straw	500	Field	4	2	Increased methanotrophs	Nan et al. (2020a)
Rice straw	500	Field	4	4	Increases in soil dissolved organic carbon, NH_4^+-N, and porosity induced larger increase of methanotrophs than methanogens in the first year suppressed the abundance of methanogens for the rest three years	Wang (2019a)

from paddy soil. Emphasis was given on the current explored mechanism of fresh biochar application on CH_4 mitigation. Furthermore, the existing results of biochar on CH_4 emission after long-term application were explored. Finally, the potential impacts of biochar aging on CH_4 emission and underlying mechanism were briefly discussed.

2 Effects of biochar application on methanogenic activity

2.1 Inhibition of methanogenic activity through decreasing dissolved organic carbon

Most of the published research studies suggested that biochar applications into paddy soil inhibit the numbers and activities of methanogens by decreasing the soil dissolved organic carbon (DOC). Soil DOCs are important substrates for methanogens and thus for CH_4 production (Conrad 2007). The high porous biochar material is composed of a large portion of recalcitrant (aromatic) C and small fraction of labile C (Zimmerman 2010). Yu et al. (2012) reported that when biochar was applied into paddy field, the soil DOC was decreased, which accounted to the adsorption via biochar pore. Similarly, Zheng et al. (2016) demonstrated that contents of DOC were significantly decreased by 52% and 71% under biochar amendment at 20 and 40 t ha^{-1}, respectively. In other study, Liu et al. (2011) conducted an experiment to explore the bamboo chip and rice straw biochar (BC and SC) amendment on CH_4 mitigation. Their result depicted that both BC and SC biochars significantly reduced CH_4 emission during incubation period by decreasing methanogenic activity derived by methanogens substrates. In addition, Han et al. (2016) also observed decreased methanogenic activity and soil DOC content when biochar was amended into paddy soil. Therefore, reducing soil DOC content as a result of biochar amendment is an important mechanism on inhibition methanogenic activity.

2.2 Inhibition of methanogenic activity through increased oxygen input

An important mechanism to inhibit the activities of methanogens in paddy soil is the high porosity of biochar that increases the O_2 flux due to its high porosity and hence increases the toxicity to methanogens. Furthermore, being a nutrient-rich source (Chen et al. 2020; He et al. 2019), biochar application into paddy soil promotes rice roots growth (Xiang et al. 2017) and thus increases O_2 secretion (Dong et al. 2013; Ma et al. 2010; Zhao et al. 2014). Consequently, the activities of methanogens and methanogenic activity are inhibited. Kim et al. (2017) examined the effect of biochar on rice yield and CH_4 emission and reported that biochar amendment increased rice yield and reduced CH_4 emission by inhibiting methanogenesis through enhancing the soil aeration and O_2 availability.

Correspondingly, biochar amendment into paddy also decreases soil bulk density and increases soil aeration and thus inhibits methanogenic activity. The responsible factor for reducing the soil bulk density is the high porosity of biochar (Waqas et al. 2018). Carvalho et al. (2014) illustrated that even 3 years application of 0.5 and 1.6% eucalyptus timber biochar into sandy loam significantly increased soil total porosity. The pot experiment of Peake et al. (2014) demonstrated that 2.5% biochar application decreased bulk density by circa 4.2 ~ 19.2%. Devereux et al. (2012) demonstrated amelioration in bulk density with biochar application rate of 5% (w/w), as Githinji (2014) observed in sandy loam and Mukherjee et al. (2014) observed in an artificially degraded soil. In addition, they also stated that methanogenic surviving cells dropped exponentially upon exposure to the increasing O_2 level in the soil as a result of biochar addition (Kiener and Leisinger 1983). The concept figure of biochar inhibition on methanogenic activity is shown in Fig. 1a.

2.3 Promotion of methanogenic activity

Few studies on soil biochar application also showed promotion of methanogenic activity. The supporting concept behind promotion of methanogenic activity is that biochar amendment increases soil NH_4^+–N (Wang et al. 2019b). Hence, the ammonia-based fertilizers promote the growth of both methanogens and methanotrophs (Wang et al. 2019b). Further, biochar application may increase rhizo deposit and plant litter as substrates for methanogens due to increased rice biomass (Banger et al. 2012). Moreover, biochar amendment also increases soil pH and is capable of ameliorating the acidic nature of paddy soil (Zhang et al. 2018). The increased soil pH is beneficial to both methanogens and methanotrophs (Le Mer and Roger 2001). However, methanotroph is more sensitive to soil pH and is promoted to a larger extent compared to methanogens (Hanson and Hanson 1996; Jeffery et al. 2016), which leads to a lower ratio of methanogens/methanotrophs. Therefore, the lower ratio of methanogens/methanotrophs will lead to the reduction in CH_4 emission. The similar case has been reported from the results of Wang et al. (2019b), who observed that both the *mcr*A and *pmo*A copy numbers were higher than the control for the first year of biochar application, while with time, the ratio of *mcr*A/*pmo*A got lower in biochar treatments than the control.

Similarly, the other methanogenic activity promotion occurred when biochar under low pyrolysis temperature (300 °C) was applied into paddy soil. In this case, biochar application into paddy would stimulate CH_4 emission rather

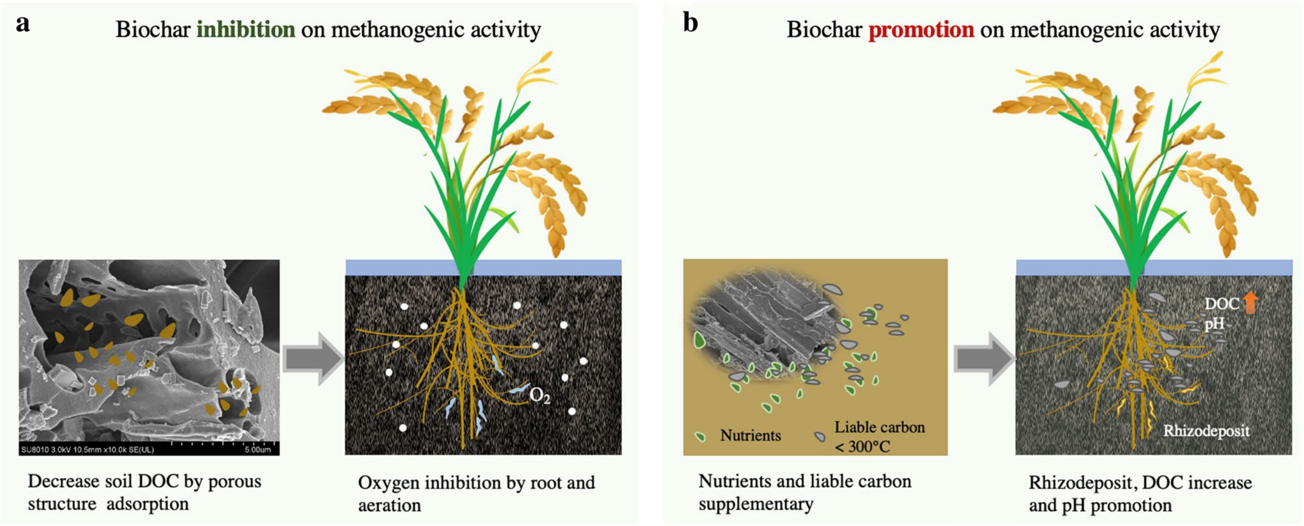

Fig. 1 Biochar effect on methanogenic inhibition (**a**) and methanotrophic (**b**) activity in the paddy soil

than mitigate. Cai et al. (2018) demonstrated that biochar produced at 300 °C significantly increased paddy CH_4 emissions in comparison to the control treatment. Conversely, the CH_4 emissions were significantly reduced when biochar was produced at 500 and 700 °C, respectively. The responsible mechanism of promoting methanogenic activity under low pyrolysis temperature is the aromatic structure that is not formed well under low temperature (<500 °C, with the high production of fulvic acids and humic acids at lower temperature (300 °C)) (Mia et al. 2017a). Therefore, biochar produced at 300 °C is largely applied to increase soil DOC and C source for methanogens (Ji et al. 2020). Singla and Inubushi (2014) reported that application of biochar produced at 300 °C significantly increased CH_4 emissions due to an increase in the soil DOC and significant growth of methanogens. In contrast, the biochar produced at elevated temperature has more stable aromatic structures (Guo and Chen 2014) and enrichment porosity (Ippolito et al. 2020), hence will not increase soil DOC due to its ability to absorb soil DOC. The comprehensive mechanism of methanogenic activity promotion as a result of biochar addition is shown in the given Fig. 1b.

3 Impact of biochar application on methanotrophic activity

3.1 Biochar impact on promoting the aerobic methane oxidation activity

Promotion of methanotrophic activity under biochar amendment has been widely recognized. This promotion mainly contributes to physical (porosity and high surface area) and chemical (alkaline nature, functional groups, nutrients supply) characteristics of biochar. The porous structure of biochar has been well reported to adsorb CH_4 and provide habitat for methanotrophs (Ji et al. 2020) and ameliorate soil aeration, thus stimulating methanotrophic activity. The alkaline nature of biochar increases soil pH to an optimum range for methanotrophs (Wang et al. 2019c). Likewise, biochar amendment as nutrients supplement also benefits the plants by increasing the rice yield increase and root growth, thus bringing more O_2 through rhizosphere (Dong et al. 2013; Watanabe et al. 1997). The figure of biochar promotion on methanotrophic activity is shown in Fig. 2.

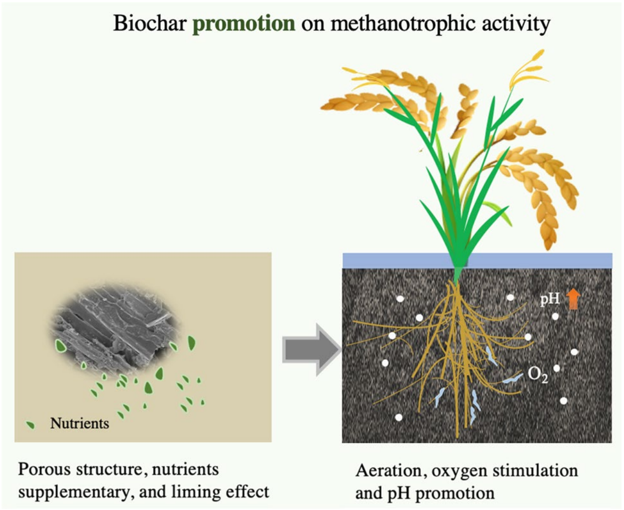

Fig. 2 Biochar effect on methanotrophic activity in the paddy soil

3.1.1 Biochar porous structure on methane mitigation responses

The high porous characteristic of biochar contributes to CH_4 adsorption and soil aeration amelioration. Rising pyrolysis temperature is accompanied with the solid matrix shrinking, various organic compounds volatilizing, and transformation of relatively large pores to smaller ones (de Melo Carvalho et al. 2014; Weber and Quicker 2018). Thus, the porosity and overall specific surface area (SSA) of biochar increases with increasing pyrolysis temperature. High porosity and large SSA of biochar exert a function of CH_4 adsorption and also provide habitat for methanotrophs (Liu et al. 2011). Further, biochar adsorption could also be benefit for nutrients retention and thus promote O_2 delivery from rice rhizosphere aerenchyma tissues. In addition, high porosity of biochar also increases the exposure of methanogens to O_2 through ameliorating soil aeration and reducing bulk density as discussed earlier (de Melo Carvalho et al. 2014; Mukherjee et al. 2014; Peake et al. 2014). The research findings of Conrad and Rothfuss (1991) on biochar application in the paddy field illustrated that 80% of produced CH_4 was consumed by methanotrophs through diffusion. Therefore, biochar porosity plays pivotal roles in enhancing aerobic methanotrophic activity in the paddy soil.

3.1.2 Liming effect of biochar on methane mitigation responses

The increase of soil pH as a result of biochar addition is another important mechanism for the promotion of methanotrophic activity. The alkaline nature of biochar is mainly due to the ash content, solid phase hydroxide and carbonate phases of biochar (Ippolito et al. 2020). In the study of Si et al. (2018), biochar when applied at the rate of 2.5 t ha^{-1} significantly increased soil pH due to liming effect. Similarly, a meta-analysis also reported that biochar application increased 11.5–11.9% of soil pH (Awad et al. 2018). Correspondingly, the optimum pH for methanotrophs is 5.0–6.5 and methanotrophs are very sensitive to the pH changes (Jeffery et al. 2016). The pH of the paddy soil is usually around 5; thus, biochar incorporation into paddy soil enhances the methanotrophic activity due to liming effect. Weber and Quicker (2018) observed a large decrease on methanotrophic when soil pH decreases from 6.3 to 5.6. Generally, at higher pyrolysis temperature, the biochar produced is higher alkaline and hence its application significantly promotes the activity of methanotrophic in acid paddy soil (Wang et al. 2014). In addition, other cooperation of liming effect of biochar with methanotrophs is lowering Al $^{3+}$ availability, thus providing protection to methanotrophs because lower pH Al $^{3+}$ is highly toxic to methanotrophs (Tamai et al. 2007). Therefore, maintaining the liming effect duration of biochar can prolong the promotion of biochar on methane oxidation activity (Jeffery et al. 2016).

3.2 Promotion of anaerobic methane oxidation activity

Recent studies explored the positive effects of biochar on anaerobic CH_4 oxidation activity induced by the electronic accepting capacities (EAC) of biochar. The surface of biochar contains various oxygen functional groups like carboxyl, carbonyl, quinone phenolic hydroxyl groups (Wu et al. 2016). The O-containing functional groups are the main entities responsible for biochar redox potential (Klupfel et al. 2014). Specifically, carbonyl and quinone are capable of accepting electron and determine the EAC properties of biochar (Zhang et al. 2019b). Thus, theoretically, carbonyl and quinone moieties can act as an electronic acceptor and consume CH_4 in the paddy. Zhang et al. (2019a) reported the anaerobic CH_4 oxidation due to the presence of quinone structure (C=O) using biochar. CH_4 anaerobic oxidation can account for 50% of the total CH_4 consumption in wetland environments (Segarra et al. 2015). Hence, biochar might mitigate CH_4 emission partly through anaerobic CH_4 consumption due to its EAC in paddy soil. Additionally, the aromatic structure of biochar can also act as a good electron acceptor due to the conjugated π-electron systems and thus may contribute to CH_4 consumption. However, the condensed aromatic structure of biochar usually formed as a result of higher pyrolysis temperature (above 700 °C), which is not usually used in paddy soil considering the agricultural ecosystem benefits (McBeath et al. 2011).

4 Long-term effect of biochar on methane mitigation in paddy soil

4.1 Short-term effectiveness of biochar mitigation responses from paddy soil

Two cases showed a short-term methane mitigation effectiveness with biochar amendment. Liu et al. (2019) conducted a six-year field observation from 2010 to 2015 and the result showed that biochar at 20 and 40 t ha^{-1} application rate reduced CH_4 emission in the first year only. Likewise, a four-year field study conducted by Nan et al. (2020a) also observed the significant CH_4 mitigation responses only for two years after the biochar application at 22.5 t ha^{-1} to the paddy soil. They also reported that no significant differences were shown in CH_4 mitigation for the following two years. The vanished CH_4 mitigation effect in the subsequent two years was ascribed to the lowered impact of biochar on methanotrophic activity. Spokas (2013) also reported that biochar aging decreased the ability to promote methanotroph activity. These studies suggested that biochar provided limited and temporary benefits on methane mitigation over a long term. To maximize the long-term CH_4 mitigation effect of biochar from paddies, the mechanism underlying the mitigation effect of aged biochar needs to be further explored.

4.2 Long-term effectiveness of biochar mitigation responses on paddy soil

Few studies reach the consensus that biochar application can mitigate CH_4 emission for a prolonged period in paddy soil. A detailed prolonged (> 4 years) research of biochar application on various soils has been conducted, which found biochar application is positive to CH_4 mitigation into paddy soil. Several trials were established in 2012 at various locations i.e., Huizhou (Qin et al. 2016), Changsha (Wang et al. 2018), Nanjing (Wu et al. 2019b), respectively. From the 4-year CH_4 mitigation effectiveness of biochar application, Wang et al. (2018; 2019c) revealed the dynamic mechanism behind this response. They reported that biochar stimulated both the methanogens and methanotrophs abundance, but with a higher promotion on methanotrophs, which caused the CH_4 reduction in the first year. However, for the subsequent three years, biochar showed an inhibition on methanogens abundance probably attributing to increased soil aeration and no effect on methanotrophs, thus mitigating CH_4 emission. These findings were in agreement with those of Wang and Qin et al. (2016), who also suggested that, three out of four years, biochar application at 5 and 20 t ha^{-1} significantly mitigated CH_4 emission. The related mechanism was roughly ascribed to promotion of methanotrophs and the improved soil aeration, bulk density and pH. In addition, in a 6-year filed experiment, Wu et al. (2019b) concluded that biochar application at 20 and 40 t ha^{-1} reduced CH_4 emission by 11.2% and 17.5% on average 6 years, respectively. However, in this study, none cumulative methane difference analysis was conducted on single experimental year. Therefore, the 6-year long-term effectiveness of biochar on methane mitigation is doubtful.

Even there exits field experiment which demonstrated 4 years of effectiveness in CH_4 mitigation with biochar application, high rate (> 10 t ha^{-1}) (Awad et al. 2018) biochar application only in the first amendment year may not prolong methane mitigation effect in paddy soil. First, CH_4 mitigation only 1 or 2 years of effectiveness of biochar application on CH_4 mitigation was also reported. Hence, long-term (> 4 years) observation of biochar amendment on CH_4 mitigation should be widely conducted. Theoretically, in terms of high-rate biochar application in single year strategy, it is hard to prolong CH_4 emission reduction effectively. First, biochar particle size must be smaller and smaller under agricultural activities and aging process (Martin et al. 2012; Mia et al. 2017a). In addition, biochar liming effect would decrease gradually, which would lose the ability to ameliorate soil pH, especially for acid paddy soil. Furthermore, biochar degradation becomes faster in paddy soil under the plant growth ambient, which means that recalcitrant carbon of biochar would change to liable carbon more quickly and with increment in amount. A nine-year study on biochar physicochemical changes and transformation from paddy soil conducted by Yi et al. (2020) demonstrated that aromatic carbon (recalcitrant carbon) of biochar decreased by 5.0% in bamboo biochar and 8.7% in rice straw biochar, respectively. Smaller biochar particle size and the gradually lost liming effect would weaken the promotion of biochar on methanotrophic activity, while the accelerated biochar degradation would enhance methanogenic activity. Hence, it is probably that, after years of aging process, biochar will lose the ability to mitigate CH_4 emission in paddy soil. However, the biochemical processes in soil and the interaction between biochar and soil biochemical factors are such complex. The actual long-term CH_4 mitigation effect exerted by biochar amendment should be further explored.

4.3 Potential impact of aged biochar on methanotrophic and methanogenic activities

Though the few studies reported short-term effectiveness of biochar on CH_4 mitigation, the mechanism behind this phenomenon is still unclear. The lower potential of biochar for CH_4 emission may also be accompanied with aging process. In paddy soil, the force of agricultural activities and crop growth accelerate physicochemical changes, plowing and tillage would expose biochar to air for oxidation and experience physical breakdown (Mia 2017a; Yi et al. 2020). Biochar would also be oxidized by O_2 secreted from crop roots (Joseph et al. 2010). Accordingly, the exploration of the mechanism should first focus on changes in biochar attributes over time in filed.

4.3.1 Changes in the porosity and its impact on methanotrophic activity

The blockage and breaking of pores on biochar surface may contribute to lowering the promotion of methanotrophic activity. As a result of continuous farming practices, such as rice growing, the biochar particles become smaller and the pore structure may be blocked or in-filling with SOM (Martin et al. 2012). As a result, the smaller size and blocked pore of biochar would probably reduce the improvement of soil aeration. This would weaken the positive promotion of biochar on methanotrophic activity. However, there are also some studies which reported that with the process of biochar aging, the porosity and SSA increased significantly. Through a 5-year field experiment, Dong et al. (2017)

found decreased average diameter of biochar pores through increasing new small pores and 98% to 114.3% increase in SSA. The increased porosity and SSA would probably increase CH_4 adsorption and thus adhere more substrates to methanotrophs. Further, the increased porosity would increase nitrogen retention ability and benefit the methanotrophs. Wang et al. (2020) also illustrated that the porosity and SSA increases lead to the maximum adsorption of NH_4^+–N. However, porous structure influences on methanotrophic activity with aging process need a comprehensive assessment.

4.3.2 Reduction in biochar liming effect and its impact on methanotrophic activity

The gradual reduction in the liming effect of biochar may contribute to lowering the activity of methanotrophs. As discussed, the alkaline nature of biochar comes from ash content composed of oxide/carbonate minerals of various elements, such as phosphorus, potassium and calcium (Ippolito et al. 2020). The ash content also acts as a nutrient supplement and is easily absorbed by the plants when dissolved in water. During rice tillering and jointing growth stage (flood period), the ash content of biochar dissolves and leaches, leading to the gradual disappearance of the liming effect (Chang et al. 2019; Lou et al. 2012). The same has been observed by a four-year study of Wang et al. (2019c) who reported that soil pH was constantly decreasing in the subsequent years. In addition, Nan et al. (2020a) also conducted a four-year field trail and observed the weak liming effect that probably lost the effect of ameliorating acid environment for methanotrophs and methanotrophic activities.

4.3.3 Biochar electronic transfer ability and its impacts on methanogenic and methanotrophic activities

Changes in oxygen functional groups during aging process affect the electronic transfer ability of biochar and thus exert difference on methanogenic and methanotrophic activities. Biochar experiences accelerated aging process in paddy than that without agricultural activities and introduces more oxygen functional groups with aging process. Various studies reported an increase of oxygen functional groups like hydroxyl, carbonyl, carboxyl, ketone and phenol groups in natural aged biochar (Cheng et al. 2008; Mia et al. 2017b; Qian and Chen 2014). It has been reported that after four months of soil incubation, biochar quinone content decreased (Mukome et al. 2014). Quinones and carbonyl mainly contribute to EAC, and phenolic OH is the main electron donating ability (EDC) source. Thus, changes in quinones and carbonyl functional group content inevitably affect methanotrophic processes (Klupfel et al. 2014; Zhang et al. 2019a). Even no studies illustrated methanogenic activity through biochar EDC in paddy system, plenty of studies have demonstrated the promotion effect through EDC of biochar in anaerobic digestion trail (Shao et al. 2019; Shen et al. 2017). The oxygen functional groups induced EDC increase may act on methanogenic activity promotion. Thus, calculation of EAC and EDC variation may help a lot on long-term methane mitigation responses of biochar revealing.

5 Prospects for future works

5.1 Necessity of long-term field experiments

As discussed, recent studies mainly focus on short-term CH_4 mitigation effectiveness of biochar application and lack the long-term field experiment observation on CH_4 mitigation effect. Currently, very few long-term (> 4 years) studies exist with controversy results of the CH_4 mitigation. To achieve the C peak in 2030 and C neutral in 2060, exploring biochar strategies that prolong CH_4 mitigation effectiveness is of great importance. Whereas, the current studies failed to underpin a pleasant strategy that guarantees stable and long-term CH_4 mitigation effect. Consequently, to provide theory basis and help with drafting the long-term stable effectiveness of biochar application on CH_4 mitigation strategy, long-term and *in-situ* field experiments focus on CH_4 mitigation from paddy should be conducted widely.

5.2 Key factors of biochar influencing methane mitigation

To figure out the exact mechanism of biochar aging process on long-term CH_4 mitigation effect, the key factors of biochar attributes on CH_4 mitigation should be specified. Currently, the mechanisms about biochar effect on CH_4 mitigation usually focus on the comprehensive responses of methanogenic and methanotrophic activities after biochar amendment. Researches can attribute CH_4 mitigation effect to methanogenic activity inhibition or methanotrophic activity promotion. The reason of biochar on methanogenic and methanotrophic activities was developed mainly on soil properties change (soil pH, DOC, bulk density and soil aeration etc.). However, detailed studies on biochar physical (porosity, surface area), chemical properties (oxygen functional groups, electronic transfer ability) and their significance on CH_4 mitigation are lacking. Combined with biochar physiochemical attributes changes during biochar aging process, the mechanism behind the long-term CH_4 mitigation effect under biochar amendment would be easier to illustrate. The specification of biochar attributes on CH_4 mitigation will also help to develop novel biochar materials and strategy management for enhancing long-term CH_4 mitigation effect.

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Declarations

Conflict of interest The authors declare no conflicts of interest.

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