JOURNAL OF ENVIRONMENTAL SCIENCES 119 (2022) 68–77

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JES JOURNAL OF ENVIRONMENTAL SCIENCES

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Biochar affects methylmercury production and bioaccumulation in paddy soils: Insights from soil-derived dissolved organic matter

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ARTICLE INFO

Article history:
Received 3 September 2021
Revised 28 January 2022
Accepted 9 February 2022
Available online 19 February 2022

Keywords:
Dissolved organic matter
Mercury
Methylmercury
Biochar
Rice

ABSTRACT

Biochar has been used increasingly as a soil additive to control mercury (Hg) pollution in paddy rice fields. As the most active component of soil organic matter, soil dissolved organic matter (DOM) plays a vital role in the environmental fate of contaminants. However, there are very few studies to determine the impact of biochar on the Hg cycle in rice paddies using insights from DOM. This study used original and modified biochar to investigate their effect on DOM dynamics and their potential impact on methylmercury (MeHg) production and bioaccumulation in rice plants. Porewater DOM was collected to analyze the variations in soil-derived DOM in paddy soils. The results showed that the addition of biochar, whether in original or modified form, significantly reduced the bioaccumulation of MeHg in rice plants, especially in hulls and grains ($p<0.05$). However, MeHg production in soils was only inhibited by the modified biochar. Biochar addition induced a significant increase in DOM's aromaticity and molecular weight ($p<0.05$), which decreased Hg bioavailability. Furthermore, enhanced microbial activity was also observed in DOM ($p<0.05$), further increasing MeHg

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https://doi.org/10.1016/j.jes.2022.02.011

production in the soil. Thus, the effect of biochar on the fate of Hg cycle involves competition between the two different roles of DOM. This study identified a specific mechanism by which biochar affects Hg behavior in rice paddy soil and contributes to understanding the more general influence of biochar in agriculture and contaminant remediation.

Introduction

Biochar is a carbon-rich porous material produced by biomass pyrolysis under an oxygen-limited environment, which is a critical soil ameliorant (Gao et al., 2020; Yuan et al., 2019; Wang and Wang, 2019). Owing to its well-developed pore structure and multifunctionality, biochar can substantially improve soil physical and chemical properties (e.g., soil porosity (Liu et al., 2019), organic matter (OM) content (Agegnehu et al., 2016), and pH (Gao et al., 2020)). It is widely used to enhance soil fertility (Glaser et al., 2002), promote crop growth (Ahmad et al., 2014), contamination control (Ahmed et al., 2016; Shu et al., 2016; Li et al., 2017), and mitigate greenhouse gas emissions (Awad et al., 2018; Li et al., 2018). Especially in the last decade, biochar has been increasingly used as a soil additive to remediate polluted soils and increase *in situ* carbon storage to deal with climate change (Arthur et al., 2015). Several critical reviews have comprehensively summarized research on biochar applications, including contaminant removal mechanisms and evaluating its usage in environmental management (Ahmad et al., 2014; Yuan et al., 2019; Beesley et al., 2011). In recent years, the manipulations of biochar to modify microstructure and surface properties have attracted much attention. By modifying the surface area, surface charge, oxygen-containing functional groups, and pore structure, the ability of biochar is enhanced to adsorb or immobilize environmental pollutants in soils, thus reducing ecological risk (Ahmed et al., 2016; Li et al., 2018; Qiao et al., 2019; Liang et al., 2021). Of the various modifications, introducing new functional groups or components such as amino groups (Ma et al., 2014), chitosan (Zhou et al., 2013; Huang et al., 2020), zero-valent iron (Qiao et al., 2019), or selenium (Wang et al., 2021) significantly improves the biogeochemical reactivity and application performance of biochar (Ahmed et al., 2016; Li et al., 2017).

Hg is recognized as a priority global pollutant because of its high toxicity, especially its organic form methylmercury (MeHg), the cause of the notorious Minamata disease in Japan decades ago (Hsu-Kim et al., 2013, 2018). In recent years, biochar and its modified forms have been illustrated as a helpful way to alleviate Hg pollution in various soil/sediment systems (Yang et al., 2021b; Zhang et al., 2018; Wang et al., 2016; Wang et al., 2019c), including rice paddy fields (Yang et al., 2021a; Shu et al., 2016; Wang et al., 2019a; Lv et al., 2021). For example, Zhang et al. (2019) added sludge biochar to soils and found an increase in MeHg in the soil matrix, whereas the bioaccumulation of MeHg in rice grains decreased by 73%. Furthermore, the bioavailability and bioaccumulation of MeHg in rice grains were significantly reduced when biochar was combined with other soil additives such as sodium nitrate (Zhang et al., 2018) and selenium (Wang et al., 2019a). Additionally, a study by Yang et al. (2021a) showed that chitosan-modified biochar effectively inhibited MeHg formation in paddy soil and reduced the Hg content in rice. In addition, selenium attached to the biochar could form covalent Hg–Se bonds with inorganic Hg (Zhang et al., 2012), sparingly soluble in environments. As a result, the formation of HgSe particles or nanoparticles will reduce the bioavailability of Hg in methylation (Dang et al., 2019). In contrast, some other studies have reported that the effect of biochar on the remediation of Hg-contaminated soil/sediment is not as good as expected. For example, Shu et al. (2016) reported that biochar application increased the MeHg content of soils. This is because biochar addition can alter the physical and chemical properties of soil and sediment (Beesley et al., 2011; Xiao et al., 2018), thereby affecting the biogeochemical processes of nutrient elements in soils or sediments (Beckers et al., 2019). These changes indirectly influence the mobility and bioavailability of Hg.

However, the effects of biochar on the mobility and bioavailability of Hg in soil/sediment systems are far more complex. Mainly, the sorption of inorganic Hg as Hg(II) onto biochar decreases the microbial methylation of Hg(II) and reduces net MeHg production. However, the changes in soil properties such as redox conditions and soil aggregation induced by biochar amendment also could cause additional Hg redistribution and transformation (Bandara et al., 2020). An excellent recent summary of biochar applications for remediating Hg-contaminated soil and sediments, which systematically analyzed the progress made in understanding the underlying mechanisms leading to the decrease of Hg bioaccumulation in plants, has been published by Yang et al. (2021b). Thus, considering the varying characteristics of biochars derived from different biomasses (e.g., plants, municipal sludge, and agricultural residue) and differences in the given environmental conditions, the effect of biochar on Hg pollution remains ambiguous. The underlying mechanisms remain unclear, which hinders a comprehensive understanding of the role of biochar in modifying Hg behavior in some specific circumstances.

From another perspective, of all the factors influencing Hg(II) methylation and further bioaccumulation, dissolved organic matter (DOM) is the most important because it impacts Hg speciation (Deonarine and Hsu-Kim, 2009; Graham et al., 2013; Mazrui et al., 2016; Bravo et al., 2017). There is a consensus that DOM, in general, can influence Hg bioavailability and methylation potential in two ways (Hsu-Kim et al., 2013). On the one hand, DOM-Hg complexes have been assumed to reduce the amount of Hg(II) available to the methylating bacteria because it is difficult for the large macromolecule to diffuse through the cell membranes (Hammerschmidt and Fitzgerald, 2004). Hydrophilic DOM-Hg complexes can decrease the

uptake and bioaccumulation in aquatic organisms such as algae. On the other hand, as an essential carbon and nitrogen source, the labile part of DOM can stimulate microbial growth (Bravo et al., 2017; Graham et al., 2013; Mazrui et al., 2016; Ortega et al., 2018). However, the relationships between Hg and DOM observed in both field investigations and the laboratory have been inconsistent, even concerning the above mechanisms. In particular, a large molecular weight of DOM with high aromaticity can stabilize nano-HgS, which is bioavailable for microbial methylation (Deonarine and Hsu-Kim, 2009). However, until now, establishing a general model to describe the interactions of DOM and Hg(II) remains a significant challenge under the constantly changing conditions of DOM. Thus, case studies in the specific environmental system such as rice paddy fields, wetlands, or peatlands need to be combined with DOM characterization to investigate the role of DOM in Hg methylation and bioaccumulation. Additionally, as biochar is increasingly produced and applied to soils worldwide, soil-derived DOM is expected to show significant changes due to biochar addition (Smebye et al., 2016; Chen et al., 2016; Zhang et al., 2017; Li et al., 2018). Biochar influences soil DOM are complex, depending on soil types (e.g., dryland and wetland) and biochar types (as determined by the nature of the raw biomass and pyrolysis temperature). There is still uncertainty, however, whether the changes of soil DOM induced by biochar addition could influence further MeHg production.

Based on the above background and concerns, we realized that soil DOM modified by biochar addition could also play an essential role in Hg behavior in rice paddy fields. In studies of the interaction between Hg and DOM in soil/sediment, porewater DOM is used as a proxy for soil DOM (Bravo et al., 2017; Graham et al., 2013; Jiang et al., 2018; Mazrui et al., 2016), rather than DOM of water extracting from the soil itself (Jiang et al., 2017). Thus, we proposed a hypothesis that biochar could induce changes in soil DOM and hence influence MeHg production and bioaccumulation in paddy soils. As a result, pot experiments of rice cultivation were conducted to validate this hypothesis in this study. The main objectives were twofold: (1) to investigate the changes in soil DOM characteristics due to biochar application, and (2) to investigate the impact of DOM properties on MeHg production in soils and the further bioaccumulation in rice. The aim was to gain an understanding of the effect of biochar application in rice paddy fields on Hg behavior via this link between carbon and Hg cycles.

1. Materials and methods

1.1. *Rice cultivation pot-experiments*

A pot experiment was conducted in this study at the greenhouse facility of Southwest University (SWU) in Chongqing, China (Fig. 1a). The pinecone-derived biochar was selected, including the original and modified form. Original biochar ($BC_{original}$) was produced by pinecones purchased from ShiKeJinNian Biotech Ltd. (Guizhou Bijie, China). From the technical information provided by this biochar producer, the modified biochar was obtained by being chemically coated to introduce selenium (BC_{mod}). Briefly, sodium selenite solution (3%, W/V) was prepared with a pH of 4.5. The original biochar and Na_2SeO_3 solution were mixed in a supercritical carbon dioxide device to react for 2 hr. The reaction conditions were speed at 120 r/min, the temperature at 40 °C, and the pressure at 20 MPa. Then the mixture was washed repeatedly with ethanol and dried in a vacuum drying oven for 12 hours to obtain selenium-modified biochar. More details of the essential characterization of the biochar are listed in the supporting information (Appendix A Table S1 and Figs. S1-3). In this experiment, the surface layer (0-20 cm) of soil was collected from the National Purple Soil Fertility and Fertilizer Benefit Monitoring Base of SWU. Based on the Chinese Soil Taxonomy, the soil is a neutral purple soil developed from the purple sandstone of the Shaximiao Formation of Jurassic age. Purple soil is classified as Regosol in the Food and Agriculture Organization taxonomy and Entisol in the United States Department of Agriculture Taxonomy. The total Hg (THg) and MeHg in the purple soils were 152.10 ng/g and 0.08 ng/g, respectively. More details of the basic physicochemical properties of the soil are listed in supporting information (Appendix A Table S2).

The soils were air-dried and passed through a 20-mesh sieve. The round waterproof polyvinyl chloride (PVC) buckets (top diameter: 24.5 cm, bottom diameter: 21.5 cm, height: 24.5 cm) were filled with 7 kg soil. Exogenous Hg as $HgCl_2$ solution was added to the pots and a control with no biochar amendment. The added soil Hg content was approximately 5 μg/g. Previous studies have shown that adding low-dose bamboo source BC (0.3%, W/W) may be cost-effective to reduce MeHg accumulation in rice (Wang et al., 2020a). Given the dual considerations of cost and repair effect, original (non-modified) biochar ($BC_{original}$) or selenium-modified biochar (BC_{mod}) were added to the pots to give 0.2% weight biochar/weight soil (Fig. 1b). In addition, 150 μg/g ammonium acetate, 100 μg/g $Ca(H_2PO_4)_2$, and 85 μg/g KCl were added as N, P, and K fertilizers to adjust the soil nutrients. The soil was flooded with deionized water during the rice cultivation process. The water surface was kept approximately 5 cm from the soil surface. After 30 days of seedling growth, two healthy rice seedlings (*Oryza sativa* L.) of similar size were transplanted into each pot. All pots were placed in a well-ventilated cultivation site (Fig. 1a), naturally lit, surrounded by protective fences, and had a waterproof transparent ceiling. The rice seedlings (commercial tag: Fengyou 210) were provided by Longping Agriculture Co., Ltd.

1.2. *Sample collection*

In this experiment, porewater samples were collected using a Rhizon sampler (Rhizosphere Research Products, Netherland) (Fig. 1c). Porewater was then filtered through a pre-rinsed 0.45 μm polyethersulfone membrane for subsequent total organic carbon (TOC) measurement and DOM characterization. Soil samples (0–20 cm depth) were harvested to investigate the changes in Hg content during the entire cultivation period. Rice plants were collected for further Hg measurements at the mature stage (110 days after seedling plantation). Soil and plant samples were freeze-dried and stored in a refrigerator at 4 °C until further analysis.

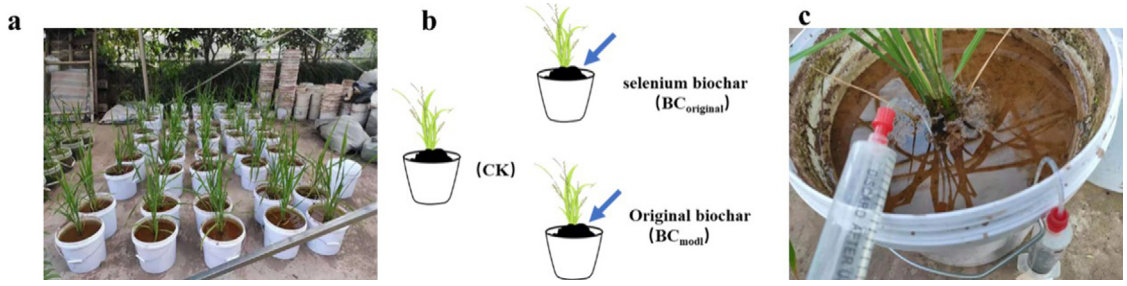

Fig. 1 – Rice cultivation pot experiments, including (a) picture of adding biochar in the rice pot experiment; (b) schematic illustration of biochar addition in the rice pot experiments (including control CK, $BC_{original}$ and BC_{mod} pots); and (c) collection of paddy soil porewater by Rhizon sampler. Porewater was extracted into the sampler under vacuum, provided using a syringe. The sampler comprises three parts: the front end is a sampling head composed of a white porous hydrophilic filter membrane (diameter 2.5 mm, aperture 0.6 μm), the middle is a transparent extension tube, and the end is a connector (used for linking syringes).

1.3. *DOM characterization*

DOM characterization was conducted in the Environmental Biogeochemistry Laboratory of Natural Organic Matter (NOM-Lab) in SWU. The DOM concentration was measured using a TOC analyzer (Shimadzu TOC-L, Japan) and expressed as dissolved organic carbon (DOC) (mg/L). All DOM samples were diluted 28 times with Milli-Q® Water (18.2 MΩ· cm) for optical analysis. Fluorescence and UV-Vis measurements were performed at a constant room temperature of approximately 25 °C using an Aqualog® absorption-fluorescence spectrometer (Horiba, Japan) to characterize the optical characteristics of the DOM. The internal filtering effect of the excitation emission matrix was corrected using Milli-Q® as a blank, and the UV-Vis absorption spectrum was obtained by scanning an adaptive cuvette with an optical path of 10 mm across the 230–800 nm wavelength range, with a scanning interval of 1 nm. The fluorescence spectrum was measured at excitation (E_x) 230–450 nm (5 nm increments), and emission (E_m) wavelength of 250–620 nm (3.18 nm increments). The Aqualog® software was automatically used to remove Raman and Rayleigh scattering during the sample analysis.

Spectral parameters were calculated based on previous studies. Specific ultraviolet absorbance ($SUVA_{254}$) refers to the absorbance of UV light in a water sample at 254 nm, which is normalized to the DOC concentration to characterize the degree of aromaticity of DOM (Liu et al., 2020). Spectral slope (S_R) is calculated as the ratio of the slope of the shorter wavelength region (275–295 nm) to the slope of the longer wavelength region (350–400 nm), which is usually inversely proportional to the molecular weight (Helms et al., 2008). The absorption coefficient (a_{355}) was chosen to quantify the abundance of the light-absorbing fraction of DOM (i.e., CDOM) (Osbum et al., 2016). The modified humification index (HIX), an indicator of the humic substance content or the degree of humification, was calculated as the peak area under the emission spectrum at 435–480 nm divided by the sum of peak area at 300–345 nm and 435-480nm, at an excitation wavelength of 254 nm (Ohno, 2002). The index of recent autochthonous contribution (BIX) was calculated by dividing the peak area at the emission wavelength of 380 nm by the peak area at 430 nm at an excitation wavelength of 310 nm (Huguet et al., 2009).

1.4. *Determination of THg and MeHg*

The THg content in soil and rice plants (i.e., roots, stalks, leaves, and grains) was measured using F-732 cold vapor atomic fluorescence spectroscopy (CVAAS, F732-S, Shanghai Huaguang Instrument Co., Ltd., China) (Zhang et al., 2010). Soil analyses used 0.1 g soil was digested with 5 mL ultrapure water and 5 mL aqua regia (HCl: HNO_3 = 3:1, V/V) in a 95 °C water bath for 5 min (Feng et al., 2009). Rice analyses used 0.1 g of rice plant samples in a water bath at 95 °C for 3 hr with 5 mL of freshly prepared mixed acid (HNO_3: H_2SO_4 = 4:1, V/V), shaken every 30 min (USEPA, 2002). The THg content of porewater was determined by oxidation, purging, trapping, and cold vapor atomic fluorescence spectrometry following the USEPA method 1631 (USEPA, 2002). For MeHg analysis, 0.2 g of soil or 0.1 g of rice plants were extracted using 25% (V%) diluted HNO_3, 1 mol/L $CuSO_4$ solution, and 25% (V%) KOH-methanol solution, respectively (Liang et al., 1996). CH_2Cl_2 was extracted and combined with an aqueous ethylated isothermal gas chromatography-cold atomic fluorescence method (GC-CVAFC, Brooks Rand model III, USA) (Liang et al., 1996). The MeHg content in porewater was determined using the distillation-ethylation method (Jiang et al., 2004).

1.5. *Quality control and statistical analysis*

Quality control for THg and MeHg determination in samples used method blanks, spike recoveries, duplicates, and certified reference material. All measurements were completed in the Mercury Biogeochemistry Laboratory (MBL) in SWU. More details of the standard operating procedure (SOP) of Hg measurements in MBL are provided in (Cheng et al., 2018). The detection limit (LOD) was estimated as three times the blank standard deviation. The method blanks were lower than the LOD values. The method LOD of THg and MeHg in soil and rice tissues was 0.01 ng/g and 0.002 ng/g, respectively, whereas LOD in porewater was 1 ng/L for THg and 0.02 ng/L for MeHg,

respectively. The following certified reference materials (CRM) were used as standards: citrus leaf (GBW10020, NRCCRM), soil (GBW07428, NRCCRM), and estuarine sediment (ERM-CC580, NRCCRM). The recoveries ranged from 85% to 110% for THg and MeHg analyses, respectively. The detailed results of the certified reference material analysis are listed in support information (Appendix A Table S3).

In this study, the net methylation potential was evaluated using the concentration of MeHg normalized to total Hg (MeHg/THg, %) in submerged soils (Liu et al., 2020). R version 4.1.0 was used for statistical analysis (R Core Team, 2021). The effects of different biochar treatments on various parameters were tested using the non-parametric Kruskal-Wallis test. Further, non-parametric *post hoc* procedures were conducted using the Kruskalmc function from the pgirmess package, when significant effects were found (Giraudoux, 2021). The error bars represent the standard error (SE), and differences were considered significant at $p < 0.05$. All drawings were obtained using the ggplot2 package (Wickham, 2016), and tabulation was performed using Microsoft Office Excel 2016.

2. Results and discussion

2.1. Characteristics of porewater DOM from paddy soils in different treatments

In general, biochar may increase the humification of soil DOM by releasing indigenous DOM and selectively adsorbing small-molecule DOM from the soil matrix. DOM release and adsorption process are the key to determining biochar's effect on soil DOM (Feng et al., 2021). Although previous studies have reported that biochar could significantly change the content and properties of soil DOM (Gao et al., 2020; Feng et al., 2021), the results are inconsistent. Some studies have shown biochar-induced elevation of DOC with increasing aromaticity and humification of soil DOM, due to the rise in soil pH induced by the biochar and biochar-derived DOM itself (Smebye et al., 2016; Zhang et al., 2017; Liu et al., 2019; Gao et al., 2020; Feng et al., 2021). In contrast, Cai et al. (2018) found that the addition of biochar decreased soil DOC concentrations by preferentially retaining high-molecular-weight and humic-like components of organic matter. In contrast, Dong et al. (2019) reported that biochar had minor effects on soil DOM in a long-term field investigation. Thus, it was necessary first to clarify the impact of biochar on soil DOM to further evaluate its potential as an environmental amendment for contaminant remediation.

In this study, DOM concentrations, shown as DOC (mg/L) in soil porewater were measured after biochar addition. Quantitatively, the DOC content in the treatment was not significantly different ($p > 0.05$) from the control (original soil without biochar), regardless of biochar type (Fig. 2a). This finding is different from previous studies, wherein distinct influences of biochar on the DOC concentrations were observed (Zhang et al., 2017; Li et al., 2018; Gao et al., 2020). The lack of effect suggests that DOC production (e.g., DOC released from biochar and intrinsic soil) was possibly offset by consumption through a process such as the re-adsorption on biochar and soils. Meanwhile, enhanced microbial growth could also increase DOM mineralization. However, in contrast to DOC, the optical analysis showed that DOM characteristics were significantly changed induced by biochar addition (Fig. 2b–k). Color DOM (i.e., a_{355}) (Appendix A Fig. S4) and $SUVA_{254}$ (Fig. 2b) were higher in the biochar treatments than in control ($p < 0.05$), but the control showed higher S_R values (Fig. 2c). These changes imply that the DOM in soil amended with biochar showed greater aromaticity, molecular weight, and chromophoric components. On the other hand, the HIX was less sensitive than $SUVA_{254}$ in indicating changes in DOM humification, but DOM associated with modified biochar treatment remained significantly higher in HIX than for the control (Fig. 2d). Furthermore, after normalization to remove the dependence on DOC concentrations, normalized CDOM (Fig. 2e) and all humic-like fluorescence peaks such as A (Fig. 2f), C (Fig. 2h), and M (Fig. 2j) were higher in the treatments than in control ($p < 0.05$), further confirming the increase in humic character of the DOM.

In addition, the BIX values were higher in the biochar treatments than that in the CK (Fig. 2k). Similar increases in BIX within elevated $SUVA_{254}$ were also reported by Gao et al. (2020). As an essential fluorescence parameter with biological implications, the BIX index was initially developed to compare M and C fluorescence peaks (Appendix A Fig. S4). The BIX correlates with the total dissolved nitrogen, indicating increased microbial productivity, leading to increased intensity of peak M, representing microbial-produced humic-like component. Thus, the increases in BIX (Fig. 2k) and DOC-normalized peak M (Fig. 2j) could be explained by the positive microbial responses (Mitchell et al., 2015) in such biochar-amended paddy soils, such as an increase in microbial abundance (Hale et al., 2015) and biomass with the soil microbial community (Hu et al., 2014; Sun et al., 2013). Conversely, the recent enhanced microbial activities reflected by BIX and peak M might imply the possibility of a positive priming effect of biochar on solid organic matter (SOM) (Luo et al., 2011). However, this effect of enhancing native SOM content could be compensated by increasing soil carbon due to biochar incorporation. As a result, in biochar treatments, DOC concentrations (Fig. 2a) and normalized protein-like components (i.e., peaks B/DOC and T/DOC) (Fig. 2g and i) were not significantly different from those in CK.

2.2. Influences of porewater DOM properties on MeHg production in paddy soils

Several previous studies have illustrated that biochar can successfully decrease MeHg production (Wang et al., 2019b; Zhang et al., 2018). In the present study, our observations were slightly different. In soil phases, the influence of the original biochar on Hg dynamics was not evident (Fig. 3a–c) because the total Hg content (THg), MeHg content, and the degree of methylation (i.e., MeHg/THg ratio) were not significantly different from those of the control ($p > 0.05$). However, only the MeHg and MeHg/THg ratios in the modified biochar treatment were significantly lower than those of the control and initial biochar treatments (Fig. 3b and c). This observation suggests that only modified biochar in this study could effectively decrease MeHg production in paddy soils. Additionally, in porewaters (Fig. 3d–f), the MeHg content was significantly lower in the biochar treatments ($p < 0.05$), which was explained by

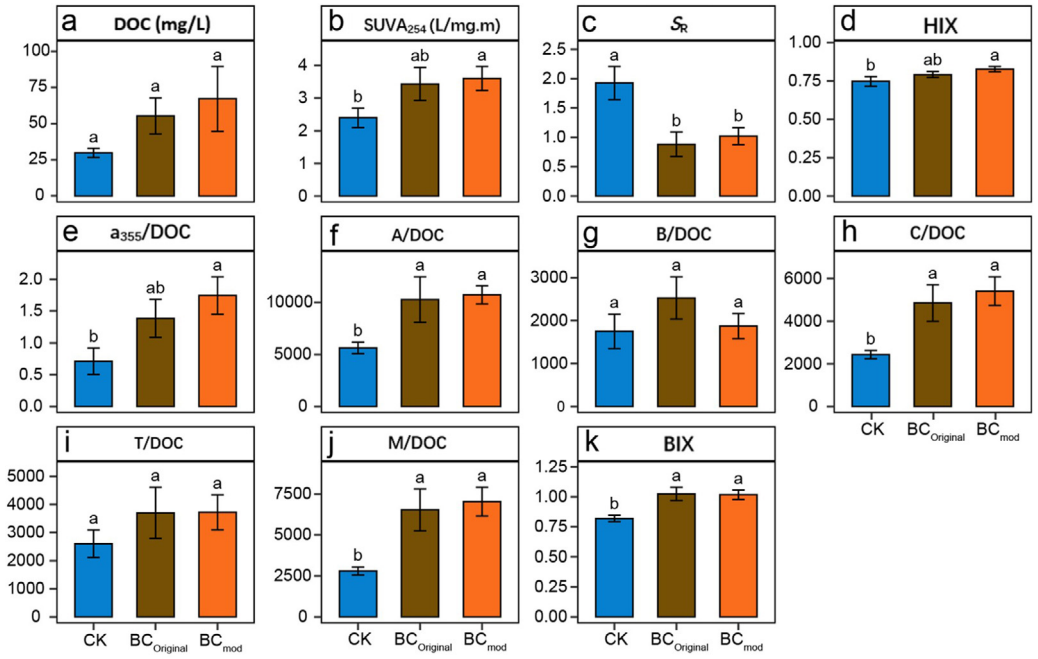

Fig. 2 – Comparisons of DOM properties in paddy soil porewater from different treatments including control (CK), original ($BC_{original}$), and modified biochar (BC_{mod}). Different letters represent significant differences ($p<0.05$) in each sub-figure for each DOM parameter among the three treatments.

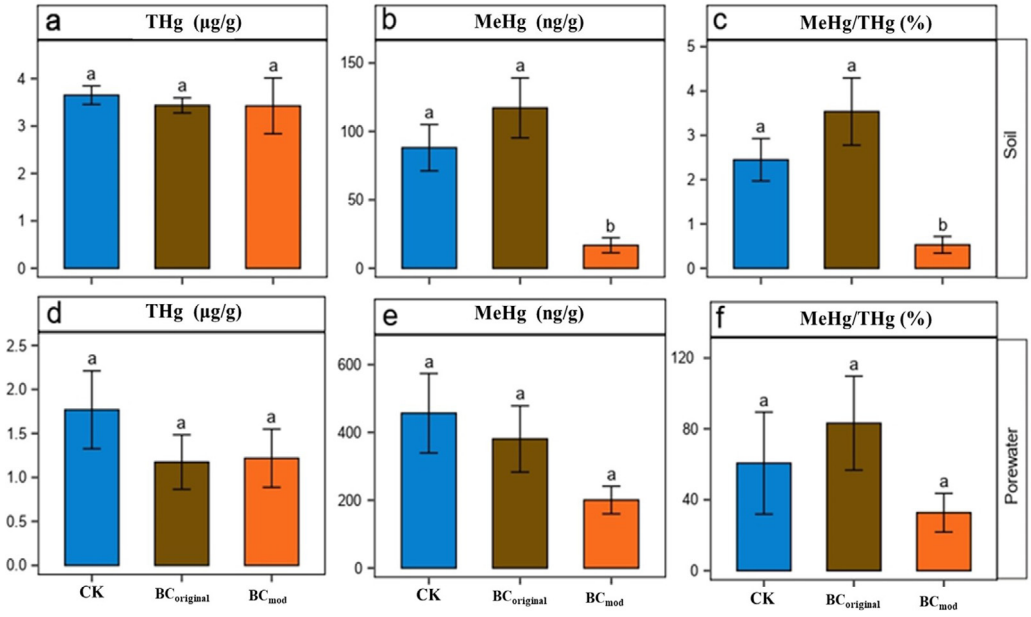

Fig. 3 – Comparison of mercury concentration and speciation (THg, MeHg, MeHg/THg) in porewater and soil for the control (CK), original ($BC_{original}$), and modified biochar (BC_{mod}) treatments. In each sub-figure, different letters represent the significant difference of each DOM parameter between the three treatments ($p< 0.05$).

the different partitioning coefficients (K_d) from soil to porewater of Hg in the different treatments (Appendix A Fig. S5). There were no significant differences between THg content and methylation degree (i.e., MeHg/THg ratio) among the three treatments.

From the insights gained from the DOM property changes induced by biochar addition, the MeHg production observed in paddy soils could be explained by two aspects of DOM in the Hg methylation process: (1) microbial activities and (2) Hg speciation (Graham et al., 2013). After biochar addition, porewater

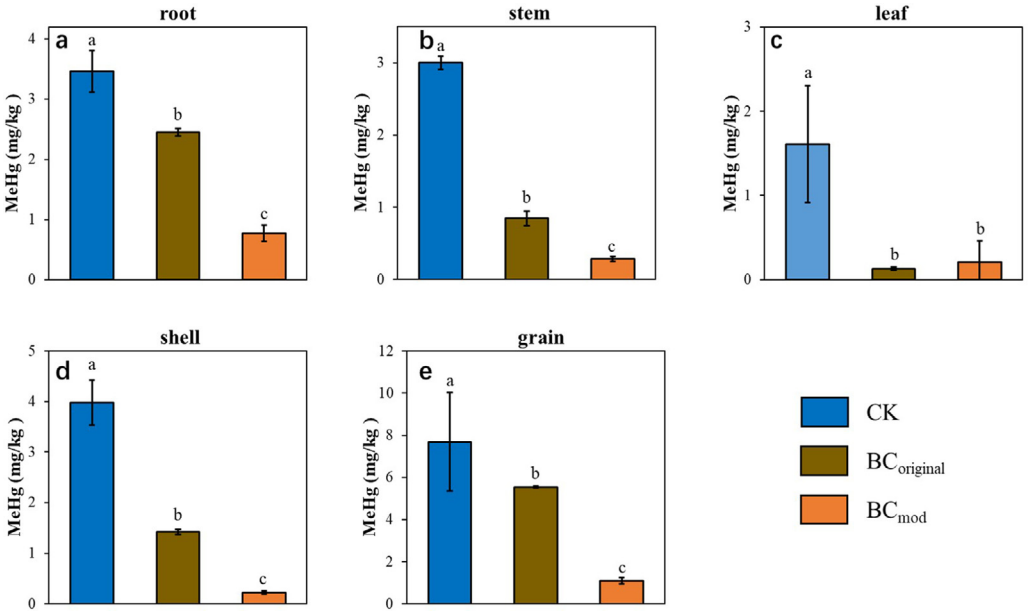

Fig. 4 – MeHg accumulations in different tissues of rice plants in the three treatments, including the control (CK), original ($BC_{original}$), and modified biochar (BC_{mod}).

DOM showed higher aromaticity and microbial signals, indicating elevated OM humification and also soil microbial activity (Fig. 2). Generally, OM with higher aromaticity, for instance refractory OM, plays a role in immobilizing Hg(II) and decreasing its bioavailability for microbes (Hsu-Kim et al., 2013; Hammerschmidt and Fitzgerald, 2004). In contrast, highly microbial-predominant components of OM (i.e., labile OM) can show enhanced microbial activity and increased MeHg production (Bravo et al., 2017; Ortega et al., 2018; Jiang et al., 2018). Thus, despite the original biochar possibly decreasing Hg(II) availability in the present study, enhanced microbial methylation could compensate for such an inhibitory effect. Additionally, it should be noted that the modified biochar was chemically modified by selenium (Se), which is renowned for its antagonistic interaction with Hg to decrease Hg bioavailability for microbes and plants (Wang et al., 2016, 2019a; Zhang et al., 2012). Thus, in this treatment, lower MeHg production indicated that enhanced microbial activity could not overwhelm the inhibitory effects induced by the modified biochar. Conversely, some studies have reported that the inhibition of anaerobes (e.g., sulfur-reducing microorganisms) by Se could be another reason to explain the decrease in MeHg production (Wang et al., 2016). However, elevated microbial activity (indicated by fluorescence peak M and BIX) of DOM observed in biochar treatments (Fig. 2g and h) suggested that microbial growth may not be retarded. Thus, such an explanation can be excluded.

2.3. *Accumulation of MeHg in rice plants*

The concentrations of MeHg rice plants were measured after the harvest. The accumulation of MeHg in rice plants was significantly decreased in both types of biochar-amended soils compared to the control (Fig. 4) ($p < 0.05$). Importantly, as the component of most concern in plants from the point of view of consumption safety and human health (Meng et al., 2014), the MeHg levels in rice hull (average 0.23±0.03 ng/g) and grains (average 1.09 ± 0.14 ng/g) were observed to be lowest in the modified-biochar treatment. Compared to the control, the original biochar also decreased the MeHg accumulation in rice hulls and grains by 64.32% and 27.96%, respectively. However, regardless of the soil treatments, either with or without biochar, the MeHg levels in grain were the highest compared to other plant tissues, especially the roots, despite MeHg accumulation in paddy soils. This observation is consistent with previous studies (Meng et al., 2011; Wang et al., 2016, 2019a), indicating that the grain is the most cumulative part of the rice plant and has important implications for public health.

Although inhibition of MeHg accumulation in rice grains was observed in this study in both biochar treatments, the underlying reasons for the explanations were not completely the same. Generally, there are three main explanations for such an inhibitory effect of biochar on MeHg accumulation in plants, including: (1) biochar enhances rice growth and promotes biomass (Qu et al., 2012), resulting in a relative decrease of MeHg, called the "biological dilution effect" (Yang et al., 2021b); (2) inhibition of MeHg accumulation by decreasing plant uptake (Cui et al., 2012; Wang et al., 2020b); and (3) decreasing MeHg production in soils by influencing microbial methylation *in situ* (Wang et al., 2016, 2019a). This study observed increases in rice yield and biomass growth in the original and modified biochar treatments. Thus, the "bio-dilution effect" might partially contribute to the MeHg decreases in rice. Importantly, soil porewater DOM showed increasing aromaticity and molecular weight after biochar addition to soils. Also combined with the solid phase of biochar as the adsorption matrix, MeHg immobilization decreased the bio-uptake of rice plants. This could also explain the lower MeHg bioaccumulation in the original biochar treatment, although the MeHg production was not substantially different from the control

(Fig. 3c). Thus, we observed lower bioaccumulation factor (BCF) values in the treatments of biochar addition than CK (Appendix A Fig. S6). Finally, the possibility of reason (3) should be emphasized. Previous studies have reported that the decrease in MeHg in rice grains due to biochar remediation was closely associated with reduced MeHg levels in soils (Meng et al., 2011; Zhang et al., 2010; Wang et al., 2016, 2019a). However, this could only explain the observation in the modified biochar treatment, which showed significantly decreased MeHg production in paddy soils (Fig. 3c).

2.4. *Implications*

Many previous studies have demonstrated the usefulness of biochar application in the amendment of Hg contamination. However, the practical effect is dependent on several factors, including the different raw biomass precursors used for biochar production. For example, we did not observe significant differences in the remedial effect between the original and modified biochar treatments ($p > 0.05$). Thus, the impact of any specific biochar needs to be evaluated carefully. We have to emphasize that the mechanisms underlying the use of biochar to remediate Hg-contaminated soils and sediments are very complex. It involves many different biogeochemical factors, including Hg speciation, microbial activities, and even phytobiological responses. However, of all factors, DOM is regarded as the most important because it can influence both reductions of methylating microbes and immobilization of Hg species (Bravo et al., 2017; Graham et al., 2013; Hsu-Kim et al., 2013; Deonarine and Hsu-Kim, 2009; Mazrui et al., 2016). Importantly, this study is not a whole-package work but only focuses on the changes of DOM nature and establishes a link to Hg behavior. Fortunately, optical indices from UV-Vis and fluorescence spectra provide information regarding the changes in DOM characteristics due to soil treatments with biochar, which is beneficial for understanding the effect of biochar application. Thus, from the angle of DOM insight, this study at least provides a possible clue to explain the potential role of DOM in such a specific Hg remediation scenario. Additionally, further studies are needed to elucidate more detailed information, such as how the changes of DOM characteristics influence Hg species. Meanwhile, the effect of biochar on the microbial communities in paddy soils (Ji et al., 2020) is a crucial factor controlling MeHg production. Thus, the influence of DOM dynamics on the soil archaeal and bacterial community analyses should also be considered for future studies.

3. Conclusions

Application of biochar, regardless of its original or modified form, can significantly decrease the bioaccumulation of MeHg in rice plants, especially in hulls and grains. However, MeHg production in soils that had undergone the two biochar treatments was not the same. Unlike Se-modified biochar, the original biochar did not significantly differ from the control in influencing MeHg production. The soil DOM (or its proxy porewater DOM in this study) was found that aromaticity and molecular weight both increase, which may decrease Hg availability. Stronger microbial signals derived from DOM were also observed, which could be explained by the possible enhancement of microbial activity due to biochar addition, which might further increase MeHg production. The net production of MeHg in paddy soils may be controlled by the tug-of-war between the decrease in Hg bioavailability and the increase in microbial activity. In a practical scenario where biochar is used, the processes by which biochar influences Hg behavior are complicated and diverse. However, from the insights of soil DOM properties, the dynamics of paddy soil DOM could provide a clue to explain the different Hg methylation in soils and the inhibitory effect on MeHg bioaccumulation in plants due to biochar addition. Importantly, this study identifies one specific possible mechanism contributing to our understanding of biochar usage in agriculture and contaminant remediation.

Acknowledgments

This research was financially supported by the National Natural Science Foundation of China (Nos. 41671469 and 41977275). Dr. Tao Jiang personally appreciates the open funding (No. PTS2020-01) from PTS Key Laboratory of Hubei Province of Institute of Environment and Health, Jianghan University. He also would like to thank the State Key Laboratory of Environmental Chemistry and Ecotoxicology (SKLECE) of Research Center for Eco-Environmental Sciences, Chinese Academy of Science (CAS), for the generous support of the open grant (No. KF2020-08). This work is also partially financially supported by the State Key Laboratory of Environmental Geochemistry open grant (No. SKLEG2021201) from the Institute of Geochemistry, Chinese Academy of Sciences (CAS). Finally, the Science and Technology Support Plan Project of Guizhou Province (No. 2019-2836) was appreciated by Guomin Xu for its support in the innovative research and developments of biochar.

Appendix A Supplementary data

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jes.2022.02.011.

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