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Mitigation of mercury accumulation in rice using rice hull-derived biochar as soil amendment: A field investigation

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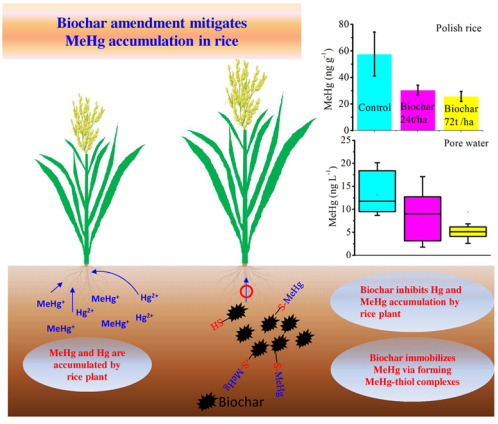
GRAPHICAL ABSTRACT



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ABSTRACT

Effect of application of 24 t ha^{-1} and 72 t ha^{-1} rice hull-derived biochar (RHB) on total Hg (THg) and methylHg (MeHg) immobilization and their accumulations by rice plants were studied in a field experiment (Wanshan Hg mine, China). The addition of two doses of RHB significantly increased the biomass of rice plants, and decreased the MeHg concentration in the pore water, as compared to the control. The RHB promoted the partitioning of pore water MeHg to the soil solid phase throughout rice growing season, and pore water THg partitioning only at rice filling stage. Mercury methylation potential was weakly affected by the RHB addition to the soil. Mercury

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might be immobilized through binding of thiols (e.g., cysteine) presented in the RHB or in the soil induced by RHB addition. Biochar addition decreased MeHg and THg contents in the tissues of rice plants, particularly in the polished rice. We attributed the reduction of THg in the rice to the bio-dilution effect, and of MeHg content in the rice to the decreased MeHg availability in the soil by RHB addition. Results suggest that RHB might be suitable for managing Hg transfer in soil-rice plants at Hg contaminated mining regions in China and beyond.

1. Introduction

Mercury (Hg) is a naturally occurring metal in our planet, but extremely toxic to humans (Beckers and Rinklebe, 2017; O'Connor et al., 2019). It can seriously affect nervous, digestive and immune systems of humans, particularly the development of the child in uterus and early in life, even with small amounts (Cherkani-Hassani et al., 2019). Mercury occurs as elemental Hg (Hg^0), Hg^{2+}, monomethylmercury (MeHg, CH_3Hg^+) and dimethylmercury (DMHg, CH_3HgCH_3) in the environment (Leermakers et al., 2005). Amongst these forms, MeHg is of the highest concern due to its bioaccumulation and biomagnification in food webs (Man et al., 2019). Mercury is listed as one of the top ten chemicals or groups of chemicals of major public health concern by World Health Organization (WHO).

Both anthropogenic and natural sources release Hg and its compounds to the environment (Wang et al., 2012a,b). It is estimated that global anthropogenic Hg emission is 2390 Mg in 2015 (Streets et al., 2019). Major anthropogenic sources include non-ferrous metal smelting, coal and oil combustion, Hg and gold production, cement production, caustic soda, steel making, municipal waste, and others (Streets et al., 2019). A widespread contamination of Hg in soils occurs through atmospheric Hg deposition, irrigation of wastewater, as well as mixing with mining wastes (Devai et al., 2005; Wang et al., 2012b). A apparent risk associated with soil contamination is the bioaccumulation of Hg in terrestrial food web, ultimately threatening human health (Liu J et al., 2019; Liu T et al., 2019). In soils, Hg^{2+} can be readily transformed to MeHg by Hg methylation bacteria (e.g., sulfate reducing bacteria) under anaerobic conditions (Beckers et al., 2019). Biogeochemical factors, including pH, redox potential, organic carbon (DOC), sulfur, and iron oxides, affect Hg methylation (Frohne et al., 2012).

There is an growing concern about paddy soil Hg contamination since rice plants can readily accumulate MeHg from soils, posing an ultimate health risk to rice consumers (Feng et al., 2008; Qiu et al., 2008). The consumption of MeHg-laden rice is a major pathway of human exposed to MeHg in inland of China (Zhang et al., 2010). Currently, there is a high demand of remedial methods for mitigating Hg risk from paddy fields in order to minimize human exposure to Hg (Wang et al., 2019a).

Methods such as phytoremediation (Marrugo-Negrete et al., 2015) and thermal treatment (Zhao T et al., 2018) have been used for Hg remediation, but they fail to attract interests of public because the former is more time-consuming and the latter is more costive and destructive, than other technologies (Wang et al., 2014). Immobilization is an effective, bearable, and applicable method that can reduce the bioavailability of contaminants in soils (Shaheen et al., 2019a,b,c). A few amendments were developed for Hg immobilization (Liu T et al., 2019; Wang et al., 2019a,b). The lack of environmentally-friendly, sustainable and effective amendments remain a main barrier for Hg remediation.

Biochar is produced through pyrolysis of biomass under limited O_2 condition, and it has been used for cadmium, copper (Salam et al., 2019), arsenic (El-Naggar et al., 2019a; Beiyuan et al., 2017a,b), lead (Li et al., 2019) immobilization in farmlands because of its benefit on soil nutrients retention, carbon sequestration, and crop yield production (Ding et al., 2016; Lehmann and Rondon, 2006; Vaccari et al., 2011). The mechanisms responsible for elements immobilization by biochar include precipitation (e.g., metal carbonate, phosphate, and (hydr)oxide precipitates), electrostatic interactions, and surface chemisorption (Park et al., 2011).

Application of biochar in Hg remediation is sparse. Results from a preliminary study showed that the addition of 1–4 % rice straw-derive biochar to contaminated soil enhances Hg methylation, but decreases MeHg accumulation in rice grains (Shu et al., 2016). Although the preliminary findings are promising, the applicability of biochar to Hg-contaminated farmlands under field conditions, particularly in Karst regions, still needs to be studied. Also, the underlying mechanisms responsible for Hg accumulation reduction in rice plants are poorly understood. However, it is well established that sulfur has a close chemical association with Hg in the environment, and its speciation changes driven by biochar addition may be involved in Hg immobilization (Liu et al., 2016; Wang et al., 2019a). Therefore we aimed to study the speciation of sulfur in both control and biochar-treated soil since it may provide insight into the role of sulfur in Hg immobilization by biochar amendment.

To extend the application of biochar in the field, and explore the Hg immobilization mechanisms by biochar, we carried out a field trial to study the amendment of two doses of rice hull biochar (RHB) (24 t ha^{-1} and 72 t ha^{-1}) on Hg bioavailability in soil, and its accumulation by rice plant throughout rice growing season at Wanshan Hg mine in China. We hypothesized that RHB addition to soil may immobilize Hg in soil, and decrease its accumulation by rice plant. Particularly, we aimed (1) to study RHB amendment on the biomass of rice plants; (2) to quantify the effect of RHB addition on the change of total Hg (THg) and MeHg in the pore water and soil; (3) to study the RHB addition on THg and MeHg distribution in the rice plants; (4) to elucidate the mechanism of THg and MeHg immobilization by the RHB in the soil as affected by the associated changes on sulfur speciation.

Result provides new insights into the mechanisms of Hg immobilization by biochar, as well as knowledge for scientists and engineers who plan to use biochar for remediation of Hg-contaminated farmlands.

2. Material and methods

2.1. Biochar production and its general properties

The studied rice hull biochar was made through the pyrolysis of rice hulls at 550 to 600℃ under O_2 limited condition in Beijing HL Biological Co., LTD (Beijing, China).

It is reported that biochar pyrolyzed at high temperature (e.g., 550 to 600℃) contained more stable carbon than that pyrolyzed at low temperature (Sun et al., 2017). Further, biochar pyrolyzed at high temperature could increase the capacity of soil to accept and/or donate electrons by controlling electron transfer reactions, enhancing redox reactions in soil (Awad et al., 2018). Biochar was transported to the experimental site and properly stored to avoid wetting by rain, prior to use. The studied rice hull biochar (RHB) contained 53 % C, 0.79 % N, and 0.09 % S (900 mg kg^{-1}). Its pH was 6.2, and electric conductivity (EC) was 120 μS cm^{-1} (Table S1).

2.2. Experimental design

Our experimental site locates at Aozhai village, Wanshan Hg mine in Guizhou province, China (E109°13′51.6″, N27°33′56.34″). The Wanshan Hg mining area (WSHM) is karstic; Hg mines are mainly associated with thin-layered and laminated fine-grained dolomite or limestone beds of the Middle unit of Cambrian age (Qiu et al., 2005).

The annual average precipitation and temperature at WSHM is 1200–1400 mm and 13–17 °C, respectively.

The experimental site covers an area of about 300 m^2. The site was cultivated by rape seed-corn-rice rotations, and ploughed at the time of adding biochar. The pH and EC of the studied soil was 6.7 and 130 μS cm^{-1}, respectively. The soil was sandy loam, and contained 3 % C, 0.32 % N, and 347 mg kg^{-1} S (Table S1). Total Hg (THg) in the soil was 39.8 mg kg^{-1}, exceeding the maximum allowable Hg content (Level III, 1.5 mg kg^{-1}) in farmlands set by the Chinese government (Chinese National Environment Protect Agency, 1995) (Table S1). MeHg content in the soil (air-dried) was 2.5 ng g^{-1} (Table S1). The experimental site was divided into three treatments with an area of about 100 m^2 for each in triplicates. The first treatment was designated as control, without RHB amendment; the second treatment was amended with RHB at a dose of 24 t ha^{-1}; the third treatment was amended with RHB at a dose of 72 t ha^{-1}. The application rates of the RHB were within the ranges recommended by a previous study (Xing et al., 2019). To be consist with the common cultivation depth (20 cm, Wang et al., 2012a) for farmlands at WSHM, the RHB was spiked to soil at a treatment depth of 20 cm by a rotary cultivator.

All plots were flooded after five days of spiking of RHB, and kept for 2 weeks prior to transplanting. The 30-day old rice seedlings were transplanted to each plot with a planting density of 800 seedlings per 100 m^2, and they were maintained for 120 days. The fertilization and pesticide application were manually conducted.

2.3. Soil and plant samples collections

Three rice plant samples and their paired rhizosphere soil samples (0 − 20 cm depth) were randomly collected from three replicates of each plot on day 52, 87, and 119 after flooding, which represents rice tillering, filling, and maturation stage, respectively (no rice plants and one soil sample were collected on day 26). Soil pore water was sampled on day 26, 52, and 87 by a sediment core method (Liu et al., 2011). Briefly, soil cores close to the roots of rice were took using plastic tubes (length: 12 cm; diameter: 2.8 cm), and sealed with caps, and they were done before rice plants sampling in order to avoid the disturbing of soil. It was not possible to sample pore water on day 116 (three days before harvest) because of drainage. Soil samples were stored in a cooler box, and rice plants were kept in nylon bags, during the transportation. Rice plants were divided into roots, stalks, leaves, and grain sections by a stainless-steel scissor, and all tissues were firstly cleaned with running tap water, and thereafter thoroughly washed using deionized water. Roots were further washed with 0.01 M ethylenediaminetetraacetic acid (EDTA) and subsequently with deionized water to remove physically attached elements. The fresh weights of leaves, stalks, and roots of rice plants were recorded using a balance with a precision of 0.01 g (BSM, Shanghai zhuojing electronic Co., China). The length of the longest root and aboveground tissue were recorded by a ruler.

Rice tissues were frozen in a deep freezer at -21°C, and subsequently freeze-dried using a lyophilizer (Fd-1-50, Beijing Boyikang Co., China) at -52°C and 14 Pa for 120 h. The dried grain section was further separated into the bran, polished rice, and hull. Plant materials were crashed to powders by an electrical crusher (IKA®-Werke GmbH & Co., Staufen, Germany), stored into Ziplock bags, and placed in a refrigerator (+4°C) prior to analysis.

Soil cores were placed in a refrigerator at +4°C, and thereafter centrifuged at 5000 rpm for 20 min to separate pore water. After centrifugation, the liquid phase was separated using a syringe, passed through a 0.45-μM micro-filter, acidified with HCl 2 %, and stored in pre-cleaned brown grass bottles. Rhizosphere soil samples were frozen in a deep freezer (-21°C), subsequently freeze-dried, and ground to 200 mesh by a agate mortar.

2.4. Sample analysis

The pH was determined in the soil suspension (soil to de-ionized water ratio of 1:2.5, w/w) by a pH meter (Hanna HI3M, Hanna instruments®, USA). Electrical conductivity was measured in 1:5 solid to water suspension. Soil particles size (< 2 mm) distribution was measured using a Malvern Mastersizer 2000 (Malvern Ltd., UK) (Wang et al., 2012a). Total carbon content in the soils was directly measured by dry combustion and thermal conductivity detection using a C/N analyzer (Multi N/C® 2100/2100S; Analytik Jena, Germany). As for sulfur analysis, soil samples were digested with concentrated HCl and HNO_3 (1:3, v/v) in a microwave system (Milestone MLS 1200 Mega, Sorisole, Italy), and the pseudo-total content of sulfur in the digested solution was determined by Inductively coupled plasma-optical emission spectrometry (USEPA 2007). As for total Hg analysis, about 0.1-0.2 g of plant or soil powders were digested with 10 mL of concentrated HNO_3 or fresh *aqua regia* (3HCl : 1HNO_3, v/v) in a water bath at 95°C for 3 h. Thereafter, 0.1 mL of BrCl was added to the digested solution, which was kept for 24 h. Total Hg in solutions were measured by cold vapour atomic fluorescence spectrometry (CVAFS) using a Hg analyzer (F732-V, Shanghai Huaguang Co., China). Total Hg in pore water samples was determined using the USEPA method 1631 (USEPA 2002). Briefly, Hg in the pore water was reduced to Hg^0, which was purged out by high purity N_2, trapped in gold trap, thermally desorbed, and detected by CVAFS using a Hg analyzer (Brooks Rand Model III, Seattle, USA).

The MeHg concentration in the pore water was analyzed using USEPA method 1630 (USEPA 2001). Briefly, MeHg in the pore water was concentrated firstly through distillation, and then added with 2 M of acetate buffer, and ethylated with 1 % sodium tetraethylborate. The MeHg was purged out from solution using high purity N_2, trapped onto Tenax traps, thermally desorbed, separated by gas chromatography, and then detected by CVAFS using a Hg analyzer (Brooks Rand Model III, Seattle, USA). As for soil MeHg analysis, 1.5 mL of 2 M $CuSO_4$ + 7.5 mL HNO_3 (25 %) + 10 mL CH_2Cl_2 were added to 50 mL centrifuge tubes containing 1 − 2 g of soil powders. The sample suspensions were kept in a water bath at 75 °C for 3 h. After heating, 2.5 mL of HCl and 9 mL of dichloromethane (CH_2Cl_2) were spiked. The suspensions were shaken using a end-over-end shaker for 30 min, and then they were centrifuged at 3500 rpm for 30 min. Phases were separated by vacuum suction, Milli-Q H_2O was added to a certain volume, and samples were heated for up to 1.5 h at 50 °C until all dichloromethane was expelled (Liang et al., 2004).

As for plant MeHg analysis, 5 mL of 25 % (w/v) potassium hydroxide (KOH)-methanol were added to centrifuge tubes containing 0.5 g plant powders. The digestion, centrifugation, separation, and heating of plant samples were done using the same procedures as for soil samples (Liang et al., 1996).

2.5. Sulfur K-edge X-ray near edge structure (XANES) spectroscopy analysis

Freeze-dried soil samples collected on day 119 from both control and 72 t ha^{-1} RHB treatments, together with sulfur reference compounds sodium dodecyl sulfate (SDS), L-cystine, L-methionine, Phenyl sulfoxide, HgS, and L-cysteine, were subjected to sulfur K-edge XANES spectroscopy analysis at medium X-ray beamline 4B7A at the Beijing synchrotron radiation facility (BSRF). All reference compounds and samples were measured in florescence mode using a fluorescent ion chamber Si (Li) detector (PGT LS30135). The K-edge of $FeSO_4$ positioned at 2482.5 eV was used for energy calibration. Spectra were collected at a stepwise interval of 0.3 eV from 2.25 to 2.6 KeV. The normalization of data was done following the method of Sun et al. (2018). The K-edge XANES spectra of the standards and samples were plotted with the energy ranged between 2.46 and 2.5 KeV.

2.6. Data analysis and quality control and assurance

Recoveries for matrix spikes ranged from 85 % to 110 % for both total Hg and MeHg in the pore water. The quality control of total Hg analysis for soil and plant were done by analyzing certified reference

materials (CRM)GBW 070009 (soil) and GBW10020 (plant), which were purchased from the Institute of Geophysical and Geochemical Exploration, China. The European Reference Material ERM®-CC580 was used for quality control for soil MeHg analysis. Since no available plant' MeHg standards, the Tort-3 (*Lobster hepatopancreas*) purchased from National Research Council of Canada was used. The certificated and measured total Hg or MeHg values in these SRMs were given in Table S2. The analysis of soil and plant's replicates showed a relative percentage difference ≤10 %.

Figures were created using *Origin* 8.0 software (Origin Lab Co., USA). *SPSS* 19.0 software (SPSS Inc., USA) was used for statistical analysis. Significant differences between the treatment groups were examined using the function of One-way analysis of variance (ANOVA) in SPSS software.

Partition coefficient (K_d) and absolute Hg mass were calculated by:

K_d (L Kg^{-1}) = Hg content in soil (mg kg^{-1})/Hg concentration in pore water (ng L^{-1}) $\times 10^{-3}$

Absolute Hg mass (g) = Hg content in the tissues of plant (mg kg^{-1}) × dry weight of tissue (kg) × 10^{-3}

3. Results and discussion

3.1. Impact of RHB on plant biomass and soil properties

Application of RHB (particularly at the highest dose) increased significantly the dry weight of the aboveground tissue (by 15–31 %) and root (by 38–83 %), as compared to the control (Figs. S1, S2), demonstrating a positive effect of the RHB on the growth of rice plant, as also indicated by others (Xing et al., 2019). This phenomena might be attributed to the ability of biochar to improve soil nutrients (e.g., phosphorus, potassium, and nitrogen) availability (Biederman and Harpole, 2013; El-Naggar et al., 2019b). However, the differences in the length of the longest root and aboveground tissue of rice plant between RHB treatments and control were statistically insignificant (Fig. S3).

Total carbon (C) contents in 24 and 72 t ha^{-1} RHB-treated soils were 37.1 % and 102 % higher than the control, which could be due to the input of C from RHB (Table S3). The pseudo-total content of S in control soil was 347 mg kg^{-1}, and increased to 379 and 364 mg kg^{-1} in 24 and 72 t ha^{-1} RHB treatment, respectively. The salinity of control soil was 132 µS cm^{-1}, and that of RHB-treated soils were 105–120 µS cm^{-1} (Table S3).The treated soil (pH = 6.56–6.65) showed a similar pH value as the control (pH = 6.55) after incubation for 119 days (Table S3), which might be because of the pH of RHB was neutral (7.09), and also might be related to the large pH buffer capacity of the studied soil.

3.2. Impact of RHB addition on Total Hg and MeHg in the soil and pore water

3.2.1. Soil

Total Hg (THg) content in all soils throughout rice growing season is shown in Fig. 1. The average content of THg in the control, 24 t ha^{-1}, and 72 t ha^{-1} RHB treatment was 44, 36, and 38 mg kg^{-1} on the end of the experiment (day 119), respectively (Fig. 1). The relatively lower THg in the 24 t ha^{-1} and 72 t ha^{-1} RHB treatments than control should be interpreted as the dilution effect with adding RHB.

The MeHg content was 4 orders of magnitude lower than THg, indicative of limited methylation potential of Hg in the studied soil (Fig. 1). Its content in the soil treated with 72 t ha^{-1} RHB was lower than both control and 24 t ha^{-1} biochar treatments after day 52 (3.5 to 4.1 ng g^{-1}), but relatively higher in the first 26 days (4.2 ng g^{-1}). This minor reduction of soil MeHg content in 72 t ha^{-1} RHB treatment indicates the inhibition of net MeHg accumulation by RHB in the soil over certain time (e.g., 52 days). The MeHg contents in the soils in control and 24 t ha^{-1} biochar treatments increased gradually from 4.4 ng g^{-1} to 5.4 ng g^{-1} after day 52 (Fig. 1). This phenomenon might be related to the enhancement of Hg methylation by root exudates at these stages (Zhao J et al., 2018), as root activities became stronger during the development of rice plant.

Mercury methylation potential (MP_{MeHg}), defined as ratio of MeHg to THg content in soil (Eckley and Hintelmann, 2006), was used to study the impact of RHB addition on MeHg production in the soil. As shown in Fig. 1, MP_{MeHg} ranged from 6×10^{-5} to 13×10^{-5} in the control soil, 6×10^{-5} to 14×10^{-5} in the 24 t ha^{-1} RHB treatment, and from 6×10^{-5} to 11×10^{-5} in the 72 t ha^{-1} RHB treatment throughout the rice growing season. Statistical analysis revealed that the differences in MP_{MeHg} between control and RHB treatments were not significant at each sampling stage, suggesting that RHB addition on MP_{MeHg} in the studied soil was minor. In contrast, Shu et al. (2016) reported that addition of 1–4 % rice straw-biochar resulted in the

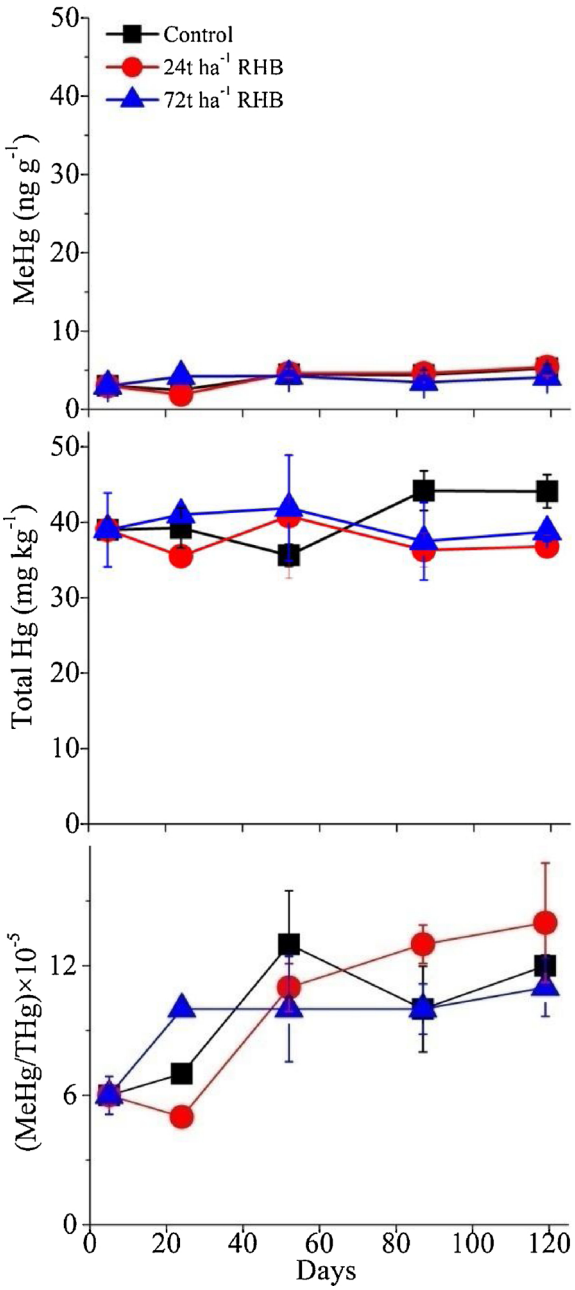

Fig. 1. MeHg and Total Hg (THg) contents, as well as their ratios (methylation potential) in both control and rice-hull biochar (RHB) treatments throughout rice growing season. note: only one soil sample was collected on day 26.

increasing of net methylation rate in a polluted soil, as the activities of sulfate-reducing bacteria (SRB) increased by biochar amendment.

3.2.2. Pore water

Application of RHB, particularly at a dose of 72 t ha^{-1}, led to a significant lower MeHg concentration in the pore water ($P < 0.05$) relative to control (Fig. 2) both at the tillering (day 52) and filling stages (day 87). However, the difference in concentration of MeHg between 24 t ha^{-1} RHB and 72 t ha^{-1} RHB treatments was statistically insignificant ($0.05 < P$) at the seedling stage (day 26). The MeHg concentrations in both 24 and 72 t ha^{-1} RHB treatments decreased by 4.0 and 1.9, 1.2 and 3.3, 1.4 and 3.0 folds, respectively, at the rice seedling, tillering, and filling stages, relative to the corresponding controls. It appears that the effectiveness of RHB at a dose of 24 t ha^{-1} became weak with the time in the soil. This phenomenon might relate to the change of surface chemistry of biochar with aging (Mia et al., 2017), weakening its effect on MeHg.

The concentrations of THg in the pore water on day 26 in the three treatments were 703 − 719 ng L^{-1}, and they decreased to 117 − 123 ng L^{-1} on day 52. The higher THg concentration on day 26 than day 52 should be related to the change of soil chemistry and plant activities, as reductive dissolution of Fe(oxyhydr)oxides released the associated Hg to the pore water after flooding (e.g., day 26) (Frohne et al., 2012) and the development of rice plant (e.g., after day 52) took up Hg from the pore water (Xing et al., 2019). Addition of the two doses of RHB has no significant impact on the pore water THg as relative to control at the rice seedling and tillering stages. However, application of 72 t ha^{-1}RHB significantly decreased THg concentration in the pore water by 2.2 times relative to control at the filling stage (Fig. 2).

The two biochar treatments increased the K_d of MeHg (Soil MeHg/pore water MeHg) at the rice seedling, tillering, and filling stages, and the extent of this partitioning was pronounced in the 72 t ha^{-1} RHB treatment at the tillering stage (Fig. 3). The impact of biochar on the K_d of THg was only clear with the high dose at the filling stage. Obviously, the RHB treatments promoted the partitioning of MeHg from pore water to soil solid phase throughout rice growing season, causing a reduction of MeHg concentration in the pore water. However, THg partitioning to soil only appears in the high dose RHB treatment (e.g., 72 t ha^{-1}) at the filling stage.

These results suggest that the RHB was more pronounced in MeHg reduction than the total Hg in the pore water, as also suggested by Gomez-Eyles et al.(2013). The apparently different effect of the RHB on MeHg and THg in the soil might be related to their different reaction mechanisms with the biochar.

3.3. Impact of RHB addition on sulfur speciation in the soil

Sulfur plays a critical role in controlling the mobility of Hg in the environment. Its organic form (e.g., thiol compounds) has a high binding affinity to Hg and MeHg (Skyllberg, 2008). Thus, we analyzed S speciation both in the control and RHB treated-soil using S K-edge XANES spectroscopy to elucidate the underlying immobilization mechanisms of Hg by RHB. The XANES spectra for the control and RHB-treated soils as well as five sulfur reference compounds (cysteine, sulfoxide, cystine, methionine, and sulfate) are shown in Fig. S4. Cysteine (electronicoxidation state of +0.5) spectra shows a distinct adsorption peak at 2473.4 eV, which originates from the transition S 1s→ σ*(S−H) (He et al., 2009); methionone spectra shows a adsorption peak at 2473.8 eV (Schroth et al., 2007); sulfoxide shows a significant adsorption peak at 2476.2 eV, corresponding to antibonding σ*(S−O) contribution (Risberg et al., 2009; Prietzel et al., 2011); sulfate (electronic oxidation state of +6) shows a adsorption peak at 2482.5 eV (Prietzel et al., 2009).

The predominate adsorption peaks in XANES spectra of the control and RHB-treated soils were similar, with a strong and relatively weak adsorption peak at 2476.2 eV and 2482.5 eV, respectively, meaning the dominant sulfur speciation in both the control and RHB-treated soils were in forms similar to sulfoxide and sulfate. Additionally, we also observed an adsorption peak at 2473.4 eV only in the RHB-treated soil, indicative of the presence of cysteine-like form. Linear combination fitting to all the sulfur reference spectra identified 7 % sulfate, 72 % sulfoxide, 8 % cystine, and 8 % methionine in control soil, and 3.3 % sulfate, 74 % sulfoxide, 6 % cystine, and 21 % cysteine in 72 t ha^{-1} RHB-treated soil (Fig. 4). The presence of a small amount of cystine and methionine in the studied soil might be sourced from the microbial decomposition of organic matter and root exudation of amino acids (Bacilio-Jiménez et al., 2003; Greenwood and Lees, 1956). The appearance of large proportion of cysteine in the RHB treated soil relative to control suggests that RHB addition induced the production of thiols (e.g., cysteine). We hypothesized two pathways might be responsible for thiol presence in the studied soil. Firstly, our biochar contained 900 mg kg^{-1} S, a certain amount of this might be thiols that being sourced from the production process. It has been demonstrated that the converting of sulfate to reduced sulfur happened in biochar during pyrolysis process in the presence of hydrocarbon molecules (in vapor and syngas) and/or H_2 (in syngas) at the pyrolysis temperatures over 500 to 600℃ (Cheah et al., 2014). Secondly, biochar can act as a "shuttle" to promote the interspecies electron transfer in the environment (Chen et al., 2014), and this process might be partially responsible for sulfate reduction to thiols. In addition, biochar addition to soil could alter the redox potential of soil. For instance, a wider range of redox potential in soil treated with biochar compared to non-treated soil has

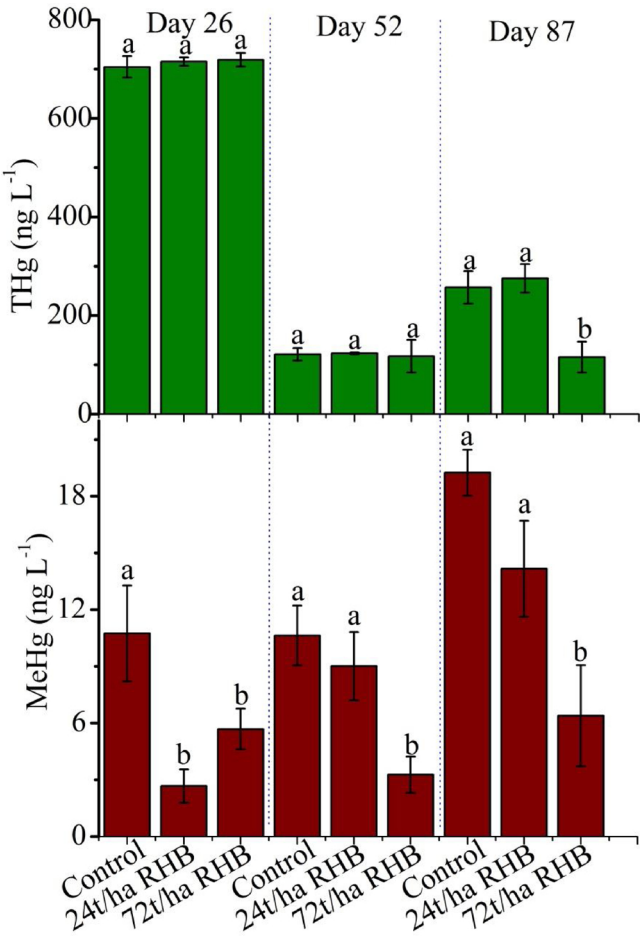

Fig. 2. Total Hg (THg) and MeHg concentrations in the pore water collected on day 26, 52, and 87, respectively, in both control and rice-hull biochar (RHB) treatments. The different lower-case letters above each bar indicates the difference between control and rice hull biochar (RHB) treatments is significant at $P < 0.05$.

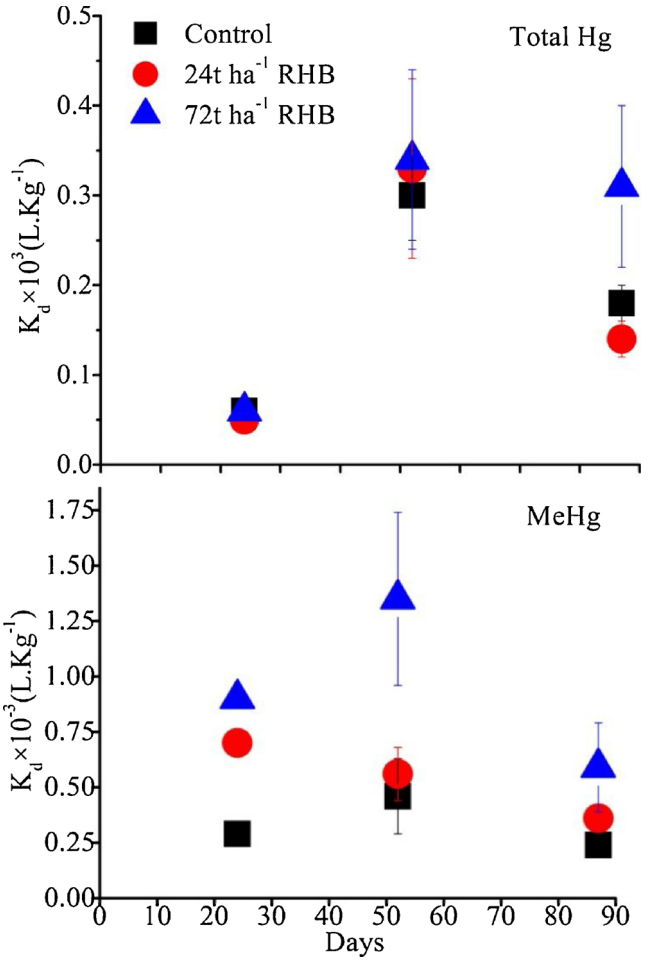

Fig. 3. The soil: water partition coefficients (K_d) for both total Hg and MeHg in control and rice hull biochar (RHB) treatments.
Total Hg: K_d (L $Kg^{-1} \times 10^3$) = Soil THg (mg kg^{-1})/pore water THg (ng L^{-1}).
MeHg: K_d (L $Kg^{-1} \times 10^{-3}$) = Soil MeHg (ng g^{-1})/pore water MeHg (ng L^{-1}).

been recorded (El-Naggar et al., 2019a). Thus, the potential impact of biochar on redox potential should influence the redox chemistry of sulfur in soils. Further studies are needed to verify those hypotheses.

3.4. The underlying Hg immobilization mechanisms by biochar in the soil

The partition of MeHg from the pore water to the soil solid phase in the RHB treatments (Fig. 3) suggests the immobilization of MeHg in the soil by the RHB amendment. The mechanisms responsible for MeHg immobilization might be linked to change of sulfur chemistry in the soil. A significant amount of thiol compounds (e.g., cysteine) was detected in the biochar-treated soil (Fig. 4), meaning that the thiols in the treated-soil likely participate in Hg immobilization reactions. Thiol has a high binding affinity to Hg in the environment (Skyllberg, 2008), and it can readily complex with both Hg^{2+} and $MeHg^{+}$ via forming -SHg and -$SHgCH_3$ bond (Huang et al., 2019a,b) to decrease the mobility of the Hg complexes (Liu et al., 2016). Thiols should be presented either in the biochar and/or soil. We thus proposed that $MeHg^{+}$ might directly bind to thiols in the biochar, or it might be firstly complexed with thiols in the soil to form MeHg-thiol complexes (Skyllberg, 2008), and then the complexes were immobilized by the biochar. Also, sorption of both Hg(II) and MeHg by biochar in a contaminated sediment has been reported (Gomez-Eyles et al., 2013).

Effect of the RHB amendment on total Hg (THg) in the pore water was less significant than MeHg. A similar phenomenon was observed by Schwartz et al. (2019) which reported that effect of activated carbon amendment on reduction of THg in pore water was less efficient than MeHg in the presence of high dissolved organic carbon (DOC) (> 30 mg L^{-1}). It was interpreted that the presence of DOC impacted THg distribution to the solid phase by reducing HgS precipitation (Schwartz et al., 2019). A previous pot experiment showed that the amendment of 72 t ha^{-1} biochar to a polluted soil could significantly increase DOC concentrations up to 50 mg L^{-1} after day 52 (Xing et al., 2019). It is likely that the amendment of RHB may increase DOC concentration in the soil, by which the partition of THg to the soil solid phase was inhibited. However, more studies are needed to clarify these processes.

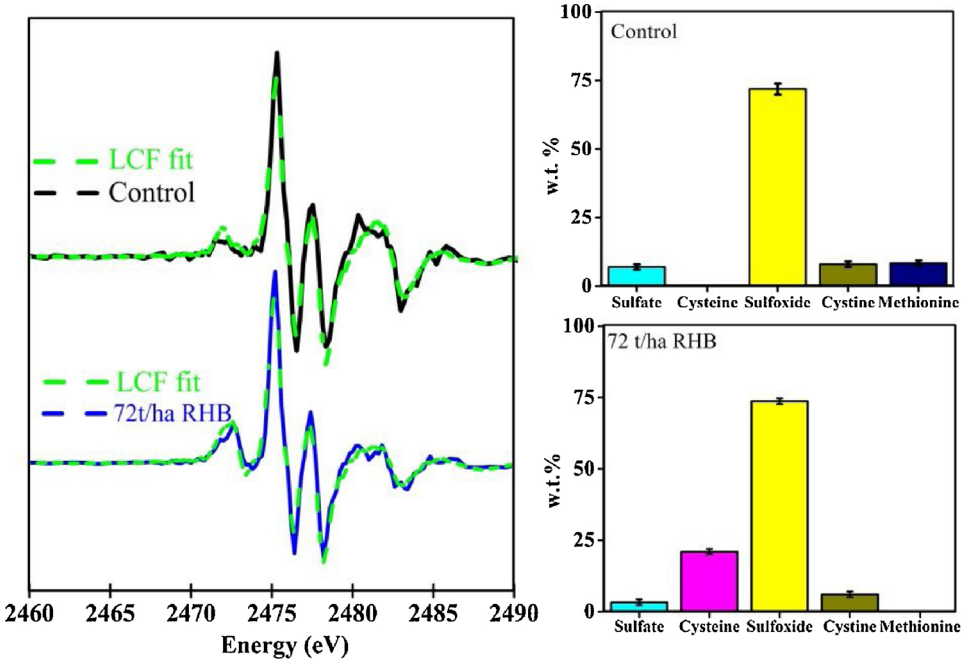

Fig. 4. The normalized first derivative of spectral of control (dark solid line) and 72 t ha^{-1} rice hull biochar-treated soil (blue solid line), and their linear combination fit (LCF) results (fittings spectral are indicated by green dash line). Linear combination fit to the control soil with 7 % sulfate, 72 % sulfoxide, 8 % cystine, 8 % methionine, and to the rice hull biochar-treated soil with 3.3 % sulfate, 74 % sulfoxide, 6 % cystine, and 21 % cysteine. The normalized sum-squared residual (NSS) is the normalized difference between two spectra expressed as $\Sigma[(y_{exp} - y_{fit})^2]/\Sigma y_{exp}^2$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.5. Effect of RHB addition on THg and MeHg distribution in the tissues and grains of rice plants

The contents of THg in the root, stalk, and leaf of rice are given in Fig. 5. The RHB amendment led to a reduction of THg contents in the roots, stalks and leaves of rice plants compared to the control plants, in particular at the filling and maturing stages. The effect of RHB amendment on THg reduction in the roots and stalks was stronger than the leaves, likely because the Hg reduction in the leaf is partially offset by its accumulation of Hg from the atmosphere (Xing et al., 2019).

The MeHg contents in the tissues of rice plants are shown in Fig. 5. We observed a significant decrease ($P < 0.05$) of MeHg contents in the roots, stalks, and leaves of rice plants in the two RHB treatments at the filling stage (day 87), as compared to the corresponding controls. The MeHg content in the stalk of rice plants in the two RHB treatments was lower than control at the tillering stage, but its contents in the leaf and root were similar. Also, MeHg contents in the roots of rice plants in the two RHB treatments were noticeably ($P < 0.05$) lower than control at the maturing stage (day 119). It appears that RHB amendment led to a decreasing of MeHg content in the rice plants, particularly at the filling and maturing stages.

Rice grains collected at the maturing stage (day 119) were divided into hull, bran, and polished rice. Mercury content in the bran could not be analyzed due to the limited biomass. The average contents of THg and MeHg were 283 and 57.6 ng g^{-1} in the polished rice in the control (Fig. 6). The 24 and 72 t ha^{-1} RHB treatments led to a 36 % and 32 %

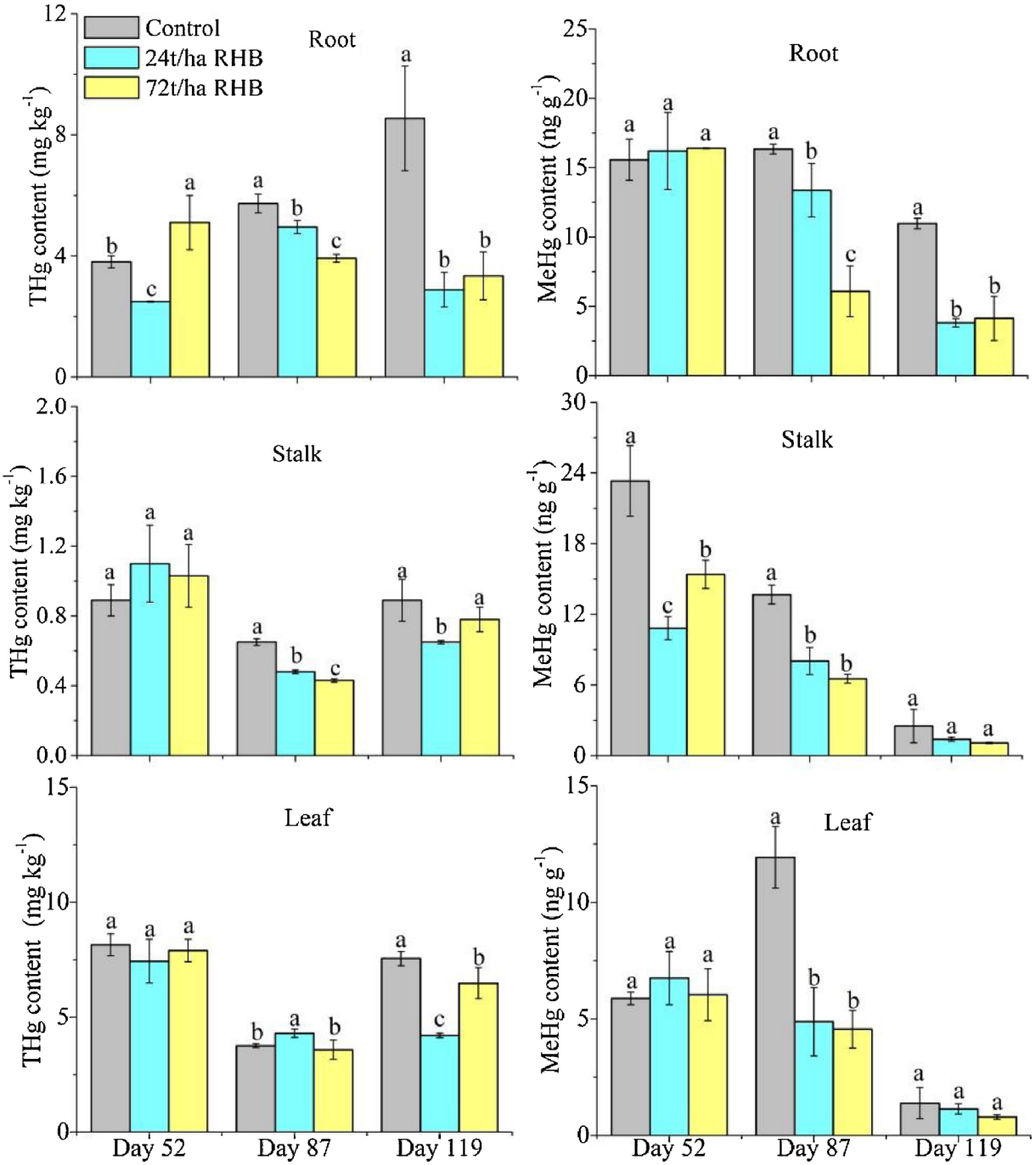

Fig. 5. Total Hg (THg) and MeHg contents in the root, stalk, and leaf of rice plants collected on day 52, 87, and 119, respectively, in control and rice-hull biochar (RHB) treatments. The different lower-case letters above each bar indicates the difference between control and biochar treatments is significant at $P < 0.05$.

reduction of THg and to a 47 % and 53 % reduction of MeHg in the polished rice, compared to the corresponding controls. Also, both THg and MeHg contents in the hull of rice plants in the two RHB treatments were significantly lower than the corresponding controls (Fig. 6).

The absolute mass of THg and MeHg in the root and aboveground tissue (stalk and leaf) of rice plant in the three treatments was calculated (Fig. S5). Application of RHB at dose of 24 t ha^{-1} resulted in a significant reduction of THg mass in the roots of rice plants collected at tillering, filling, and maturing stages, as compared to the corresponding controls; however, its high application dose (e.g., 72 t ha^{-1}) didn't significantly affect the absolute mass of THg. The THg mass in the aboveground tissues of rice plants in the three treatments was similar at the tillering and maturing stages. It appears that the high dose of RHB amendment didn't significantly decrease THg mass in the aboveground tissues and roots of rice plants. However, an opposite phenomena of reduction of THg contents in the stalk and leaf of rice plants in the RHB treatments relative to control at the filling and maturing stages was observed (Fig. 5). Meanwhile, the biomass of aboveground tissues and roots increased with RHB amendments. We explained that THg reduction in the tissues of rice plant in the RHB treatments might be a consequence of bio-dilution. Unlike THg, application of RHB at two doses noticeably ($P < 0.05$) reduced MeHg mass in the roots and aboveground tissues of rice plants as compared to control, which means a reduction of MeHg accumulation in the tissues of rice plants by the RHB amendment. We observed a significant correlation between pore water MeHg concentration and root MeHg content ($r = 0.80$, $P < 0.05$), and leaf MeHg content ($r = 0.81$, $P < 0.05$), respectively (Table S4), suggesting that rice plant MeHg was mainly sourced from the pore water. Therefore, MeHg content reduction in the rice plants was likely a consequence of reduction of MeHg in the pore water.

4. Conclusions and environmental applications

Under field condition, the addition of rice hull biochar (RHB) showed promising results in increasing the biomass of rice plant, decreasing MeHg concentrations in the pore water, and MeHg accumulation in the tissue of rice plants particularly in the polished rice. The primary mechanism of MeHg reduction by the RHB might be related to the complexation of MeHg with thiols in the soil, and enhancing the partition of MeHg from pore water to the soil. The RHB amendment also decreased total Hg concentrations in the tissues of rice plants, and the mechanism should be linked to the bio-dilution effect. The RHB was more effective in remediation for MeHg than total Hg, which might be related to the different reaction mechanisms of the RHB and MeHg/total Hg.

The change of land use types from paddy field to dry land has been proposed to be an effective solution to mitigate MeHg risk from paddy field. However, the implementation of this strategy is often hardly possible or at least a challenge since it has significant impacts on the agro-ecosystem as well as on social aspects. Also, it is controlled by climatic conditions, and education and willingness of land owners. Large areas of land are still kept for rice cultivation at Wanshan Hg mine in China until now. Here, we proposed to use biochar to reduce the transfer of Hg from

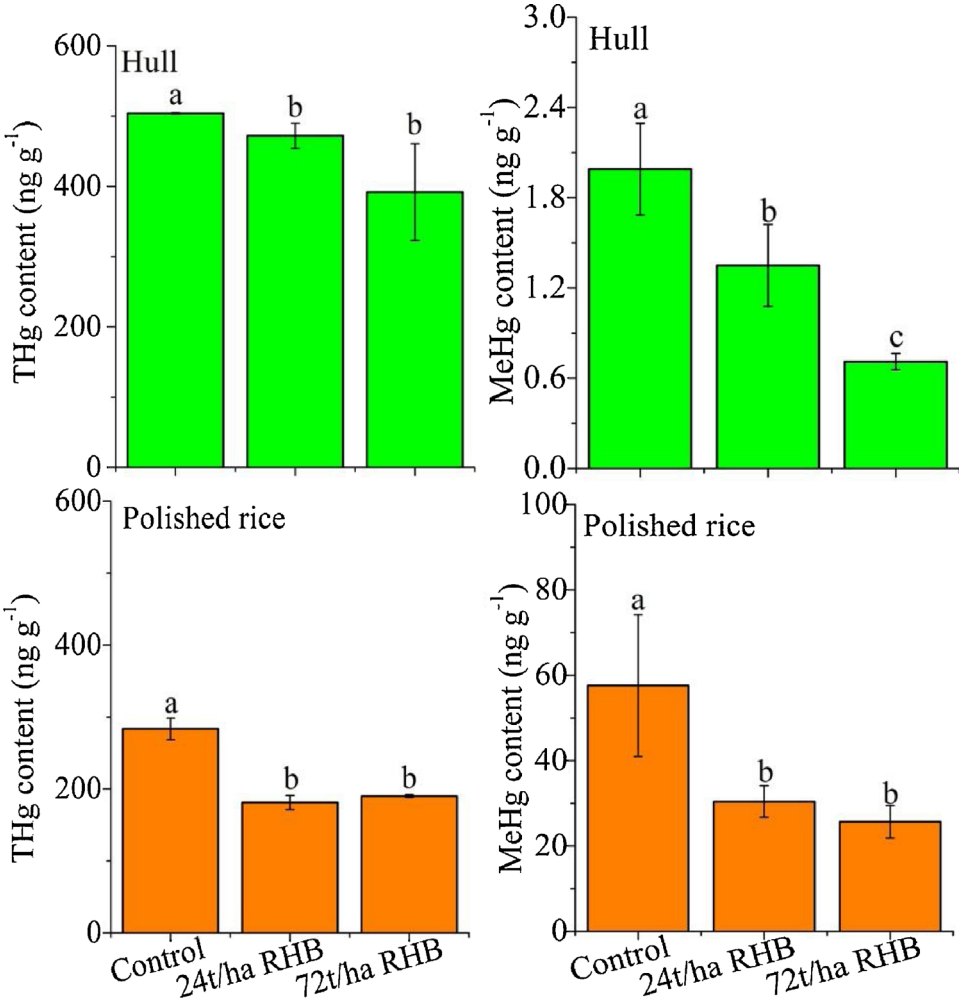

Fig. 6. Total Hg (THg) and MeHg contents in the rice hull and polished rice of rice plants collected on day 119, in control and rice-hull biochar (RHB) treatments. The different lower-case letters above each bar indicates the difference between control and biochar treatments is significant at $P < 0.05$.

soil to rice in paddy fields. The benefits such as increased biomass and rice grain yield might attract land owners to use biochar as an amendment to improve the rice grain production, and at the same time achieving the remedial aims of reducing Hg accumulation in rice grains, by which alleviating the extent of Hg exposure to the rice consumers. In this way, we may build up a practical strategy to manage the Hg risk in paddy fields at heavily polluted sites in China. The strategy may be applicable at locations in Asia (e.g., Indonesia, Philippines) where Hg contamination in paddy fields becomes a primary environmental concern due to the extensive artisanal gold mining activities.

Effect of biochar on Hg immobilization seems to be affected by the biochar properties (e.g., feedstocks, and pyrolysis temperatures). For instance, application of fallen pinecones derived biochar at a pyrolysis temperature of 200 and 500 ℃ to soil had no effect on Hg mobilization and methylation in soil (Beckers et al., 2019). Also, some biochars may increase the mobilization of toxic elements in soils such as arsenic, cadium, copper, nickel, and zinc (El-Naggar et al., 2018; Shaheen et al., 2019a). For future studies, we suggest to test various biochars originates from different feedstocks, and to evaluate their effectiveness in Hg remediation in the laboratory, greenhouse and field. Also, future studies are required to study the behaviour of Hg, particularly Hg methylation, in biochar-treated soil under systematic change of redox conditions, to gain more knowledge for establishing an optimal immobilization method.

CRediT authorship contribution statement

Ying Xing: Investigation, Writing - original draft, Writing - review & editing. **Jianxu Wang:** Investigation, Data curation, Conceptualization, Supervision. **Sabry M. Shaheen:** Writing - original draft, Data curation. **Xinbin Feng:** Resources, Conceptualization. **Zhuo Chen:** Resources, Methodology. **Hua Zhang:** Resources, Supervision. **Jörg Rinklebe:** Supervision, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jhazmat.2019.121747.

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