Science of the Total Environment 619–620 (2018) 384–390

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

# Biochar and nitrate reduce risk of methylmercury in soils under straw amendment

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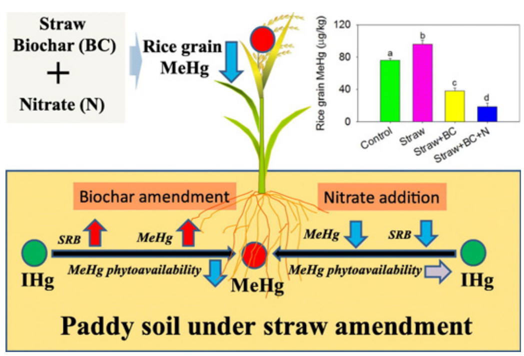
## HIGHLIGHTS

- Straw amendment increased MeHg concentrations in rice plants.
- Nitrate addition could help reduce net MeHg production in soils.
- Biochar reduced MeHg phytoavailability and bioaccumulation in soil-rice systems.
- Nitrate addition reduced microbial MeHg production by inhibiting activities of sulfate reducing bacteria.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 30 July 2017
Received in revised form 6 November 2017
Accepted 9 November 2017
Available online xxxx

*Keywords:*
Paddy soil
Methylmercury
Straw return
Bioaccumulation
Rice

## ABSTRACT

There is growing evidence that incorporating crop straw into soils, which is being widely encouraged in many parts of the world, could increase net methylmercury (MeHg) production in soils and MeHg accumulation in crops. We explored the possibility of mitigating the risk of increased MeHg levels under straw amendment by transforming straw into biochar (BC). Greenhouse and batch experiments were conducted, in which soil MeHg concentrations, MeHg phytoavailability and accumulation in rice, dynamics of sulfate, nitrate and abundances of sulfate reducing bacteria (SRB) were compared in 'Control' (Hg contaminated soil), 'Straw' (soil with 1% rice straw), 'Straw + BC' (soil with 1% straw and 1% biochar), and 'Straw + BC + N' (soil with 1% straw, 1% biochar and 0.12% nitrate). Our results indicate that straw amendment increased MeHg concentrations in soils (28–136% higher) and rice plants (26% higher in grains, 'Straw' versus 'Control'), while co-application of biochar with straw reduced grain MeHg levels (60% lower, 'Straw + BC' versus 'Straw'). This could be mainly attributed to the reduced MeHg availability to rice plants (phytoavailability, extraction rates of MeHg by ammonium thiosulfate) under biochar amendment (64–99% lower, 'Straw + BC' versus 'Straw'). However, biochar amendment enhanced soil MeHg levels (5–75% higher, 'Straw + BC' versus 'Control'). Interestingly, nitrate addition helped reduce soil MeHg concentrations (11–41% lower, 'Straw + BC + N' versus 'Straw + BC') by facilitating nitrate reduction while inhibiting SRB activities. Subsequently, addition of nitrate with biochar, compared with biochar alone, further reduced grain MeHg levels by 34%. Therefore, straw biochar together with nitrate could possibly be effective

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https://doi.org/10.1016/j.scitotenv.2017.11.106
0048-9697/

in mitigating the risk of MeHg under straw amendment. Furthermore, the results evidence the impacts of straw management on the risk posed by MeHg in soils and emphasize the necessity to carefully consider the straw management policy in Hg-contaminated areas.



## 1. Introduction

Recently, there is increasing evidence that straw return, a common way of organic matter put into farm soils, could facilitate transformation of inorganic mercury (IHg) to the more toxic and bioaccumulative methylmercury (MeHg) species (H.K. Zhu et al., 2015; Windham-Myers et al., 2014a; Strickman and Mitchell, 2017; Y.R. Liu et al., 2016). For instance, amendment of crop straw into soils was reported to increase soil MeHg levels by 19–33% (Zhu et al., 2016), 29–78% (Shu et al., 2016a), 25–91% (Y.R. Liu et al., 2016), and 20–669% (Windham-Myers et al., 2014a). Consequently, elevated MeHg levels have been found in rice under straw amendment (Zhu et al., 2016). Considering that rice consumption has recently been demonstrated to be an important pathway of dietary MeHg uptake (Zhang et al., 2010a, 2010b), the enhanced MeHg accumulation in rice under straw amendment could intensify concerns about human exposure to MeHg (Zhang et al., 2010b; Meng et al., 2010; Windham-Myers et al., 2014a, 2014b). Straw amendment is being encouraged globally to reduce air pollution (compared with straw burning) and increase soil fertility (Mandal et al., 2004; Tirol-Padre et al., 2005; Ladha et al., 2004); thus, mitigating the risk posed by higher MeHg concentrations in straw amended farming soils is of great importance.

In the last decade, there has been increasing interest in using biochar to immobilize metals and remediate metal-contaminated soils (Shu et al., 2016b; Jiang et al., 2012; Khan et al., 2013; Bian et al., 2014). This is partly because of the high surface areas and the abundance of metal binding sites in biochar (Cao et al., 2009; Gomez-Eyles et al., 2013; P. Liu et al., 2016). For Hg, a few recent studies indicate that straw-derived biochar could immobilize IHg and MeHg in soils and sediments (Shu et al., 2016b; Liu et al., 2017) and biochar amendment has been shown to reduce MeHg accumulation in plants (e.g., rice and mustard, Shu et al., 2016a, 2016b). For instance, Shu et al. (2016b) recently reported that straw biochar amendment could reduce MeHg levels in rice grains by 49–92%. Furthermore, a XANES (X–ray absorption near edge structure) study provides novel insight into the possible mechanisms of Hg-biochar binding: Hg was bound strongly with S in high-S content biochar, but bound to O and Cl in low-S biochar (P. Liu et al., 2016). Therefore, the use of straw biochar may be a promising approach to reduce straw amendment-induced MeHg bioaccumulation in plants.

While biochar was shown to effectively immobilize MeHg in soils (Shu et al., 2016a, 2016b), it should be noted that straw biochar increased net production of MeHg in soils at the same time (33–306% higher), probably through increasing supply of electron acceptors (i.e., sulfate) for microbial methylators. This together with the high concentrations of electron donors produced following straw decomposition/transformation in soils (e.g., acetate), could possibly result in elevated microbial MeHg production in soils amended with both straw and straw biochar. To reduce the side effects of biochar amendment on soil MeHg levels, there is a need to decrease the activities of SRB (Zeng et al., 2016). In this regard, nitrate could be a potential candidate to be amended together with biochar. Nitrate addition, which could facilitate nitrate reduction while simultaneously inhibiting sulfate reduction, has been widely documented to inhibit SRB activities (Greene et al., 2003; Zhang et al., 2015). Therefore, we hypothesize that co-application of nitrate with biochar may help reduce soil MeHg levels and further decrease MeHg accumulation in rice under straw amendment.

This study therefore aims to address two important questions about controlling the potential risk posed by MeHg in straw amended soils: (1) Can MeHg accumulation be reduced in rice under straw amendment, using biochar and/or nitrate addition? If so, (2) what are the underlying mechanisms? To achieve these goals, greenhouse experiments (i.e., pot experiments) together with batch experiments were carried out: (1) Soil MeHg levels and MeHg accumulation in rice following straw, straw + biochar, and straw + biochar + nitrate amendment were compared in pot experiments; and (2) the variation in MeHg mobility and availability to rice plants (i.e., phytoavailability, quantified as percentage of MeHg extractable by ammonium thiosulfate), sulfate and nitrate reduction, and SRB activities were monitored through time in batch experiments. Results from this study might help control the risk posed by increased MeHg accumulation under straw amendment and improve our understanding of Hg biogeochemistry in contaminated soils.

## 2. Materials and methods

### 2.1. Soil, rice straw and biochar

Surface soil (0–20 cm) was collected from a Hg-contaminated paddy field located in Xunyang County, Shaanxi Province, China, and is referred to as XY soil. Xunyang is one of the biggest Hg mining areas in China (Qiu et al., 2012). The XY soil was air-dried, ground and sieved through 2-mm mesh, and used in both pot and batch experiments. The total Hg (THg) and MeHg concentrations in the soil were 33,200 ± 400 and 6.0 ± 0.1 μg/kg, respectively. Low-Hg rice straw (THg: 30.9 ± 0.2 μg/kg, MeHg: 2.7 ± 0.1 μg/kg, to minimize straw amendment-induced Hg input) was collected from Yixing City, Jiangsu Province, China, rinsed thoroughly with deionized water, oven-dried, ground and sieved through 0.28-mm mesh and used for soil amendment and biochar production. Straw biochar was produced from rice straw by pyrolysis at 600 °C for 2 h under oxygen–limited conditions (Shu et al., 2016b), ground into powder and sieved through 0.28-mm mesh (similar to above). Concentrations of THg and MeHg in the biochar were 14.1 ± 0.1 μg/kg and 0.3 ± 0.01 μg/kg, respectively. The other characteristics of the soil and biochar are listed in Table S1 (Supplementary information). Chemicals and containers used in this study are described in Supplementary information, text.

### 2.2. Pot experiments

Pot experiments, in which rice was planted in XY soil amended with or without rice straw, straw biochar and nitrate, were conducted to explore the possibility of reducing MeHg accumulation in rice under straw amendment using biochar and/or nitrate addition. A total of four treatments were carried out in triplicate, i.e., (1) 'Control', i.e., XY soil; (2) 'Straw', i.e., XY soil amended with 1% of rice straw (10 g straw/kg soil); (3) 'Straw + BC', i.e., XY soil amended with 1% of straw and 1% of straw biochar; (4) 'Straw + BC + N', i.e., XY soil amended with 1% of straw, 1% of biochar and 0.12% of nitrate (1.215 g $NaNO_3$/kg soil). Since we mainly focused on investigating ways to mitigate risk of MeHg under straw amendment, effects of adding biochar alone on Hg dynamics in soils were not investigated, but it was reported in our previous study (Shu et al., 2016b). On day 0, 2 kg of XY soil was amended with straw, biochar or nitrate, added with basic fertilizer