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Biochar Amendment to the Soil Surface Reduces Fumigant Emissions and Enhances Soil Microorganism Recovery

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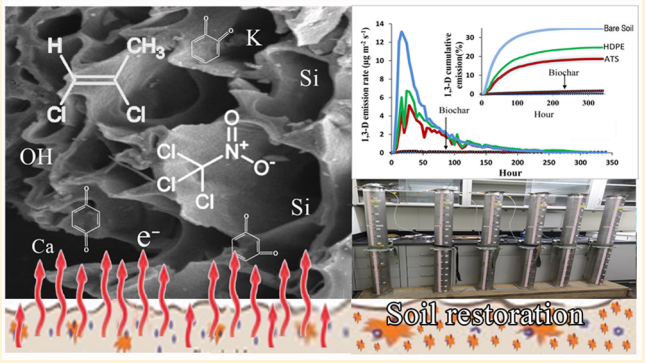
Supporting Information

ABSTRACT: During soil fumigation, it is ideal to mitigate soil fumigant emissions, ensure pest control efficacy, and speed up the recovery of the soil microorganism population established postapplication. However, no current fumigant emission reduction strategy can meet all these requirements. In the present study, replicated soil columns were used to study the effect of biochar derived from rice husk (BR) and green waste (BG) applied to the soil surface on 1,3-dichloropropene (1,3-D) and chloropicrin (CP) emissions and soil gas distribution, and on microorganism population re-establishment. Relative to fumigated bare soil (no emission reduction strategy), high-density polyethylene (HDPE), and ammonium thiosulfate (ATS) treatments, BR gave dramatic emission reductions for both fumigants with no obvious emission peak, whereas BG was very effective only for 1,3-D. With BR application, the concentration of fumigant in the soil gas was higher than in the bare soil and ATS treatment. After the soil column experiment, mixing the BR with the fumigated soil resulted in higher soil respiration rates than were observed for HDPE and ATS treatments. Therefore, biochar amendment to the soil surface may be an effective strategy for fumigant emission reduction and the recovery of soil microorganism populations established postapplication.



INTRODUCTION

Agricultural fumigants are considered critical for the control of soil borne pests in high-value crop production systems. 1,3-Dichloropropene (1,3-D) and chloropicrin (CP) are the major chemicals replacing the banned MeBr,[1] and both are highly regulated (e.g., in California) in order to limit the release of volatile organic compounds that are toxic and may also form ground-level ozone.[2,3] Field and laboratory studies have shown that 1,3-D and CP emissions can be reduced by applying agricultural chemicals such as ammonium thiosulfate (ATS), which promotes the chemical degradation of these fumigants via dehaolgenation, or by covering the soil surface with plastic tarps such as polyethylene film.[4,5] However, agricultural tarps are expensive (compared to the use of agricultural chemicals) and present difficulties in terms of disposal.[6] Application of organic wastes (e.g., animal manures) to the soil surface is known to stimulate soil microbial activity, which could potentially lead to accelerated fumigant degradation and reduced fumigant emissions.[7] However, concerns relating to strong odors from such materials may hinder the field adoption of this technique.[8] In general, the identification and assessment of low-cost, environmentally benign emission reduction strategies for fumigated fields is an important research topic, particularly if such strategies also provide soil/environmental benefits. Furthermore, the recovery of soil microbial communities following fumigation has, so far, not been considered in relation to assessing fumigant emission reduction strategies. It is ideal to mitigate soil fumigant emissions, ensure pest control efficacy, and speed up the recovery of the soil microorganism population established postapplication. However, there is currently no fumigant emission reduction strategy that can meet all of these requirements.

Biochar is a carbon-rich material produced during the pyrolysis of biomass, and its incorporation into soil has received increasing attention due to its ability to sequester carbon that would otherwise be rapidly transferred back into the atmosphere upon decomposition of the biomass.[9] Thus, biochar use has the potential to help mitigate climate change by reducing the release of CO_2.[10] Moreover, biochar has a number of beneficial impacts on soil properties (e.g., soil structure, moisture retention, nutrient retention, and microbial proliferation). It is well documented that many biochars have surfaces that can absorb a range of volatile gases.[11] Many researchers

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have also reported that biochar can reduce emissions of other greenhouse gases, such as nitrous oxide, from soils.[12,13] The application of biochar to soil therefore offers a number of soil/environmental benefits and can be economically feasible;[14,15] thus, it has the potential to become a widely used and effective management strategy for waste biomass material. In this work, we aimed to determine whether such use could also offer benefits in terms of fumigant emission reduction. For soil fumigants, the research results of Wang et al.[16] showed that topsoil application of biochar derived from wood can reduce 1,3-D emissions. Graber et al.[17] demonstrated that biochar derived from corn straw mixed with soil has substantial sorption capacity for 1,3-D.

Most fumigants are known to have a broad biocidal activity; consequently, soil fumigation treatments often involve drastic qualitative and quantitative changes in the soil environment which are likely to affect soil microbial communities and associated functions.[18] The recovery of soil microorganisms after treatment with a fumigant is critical for the development of healthy soils.[19] Many researchers have shown that biochar may indirectly stimulate soil organisms by offering an excellent habitat within its porous structure,[20,21] and reducing the bioavailability of various soil toxins through sorption.[17,22] However, Zhang et al.[23] showed that no significant treatment effects were found on the total nematode abundance when biochar addition was practiced.

In general, research on the efficiency of biochar in reducing soil fumigation emissions and aiding the recovery of soil microbes is very limited. Often, 1,3-D and CP are applied together to enhance pest control. To date, the effects of biochar amendment to soil on soil-air emissions of coformulations of 1,3-D and CP and postfumigation soil microorganism recovery have not been reported. Moreover, the effectiveness of biochar in this regard has not been compared with other, more commonly used, fumigant emission reduction strategies. The objectives of this study were to (1) determine the potential of surface-applied biochar derived from rice husk (BR) and green waste (BG) to reduce 1,3-D and CP emissions compared to a bare soil; (2) carry out a comparative study using the more common methods of fumigant emission control, ATS application and HDPE covering; and (3) determine the impact of mixing the biochar into the soil postfumigation on microorganism recovery.

MATERIALS AND METHODS

Materials and Chemicals. A stock solution of 1.45 mg μL^{-1} Pic-Clor 60 (~60% chloropicrin; 40% 1,3-D; 50:50 *cis*-1,3-D/*trans*-1,3-D ratio) was donated by Dow Agrosciences (Indianapolis, IN). The ATS was obtained from Sigma-Aldrich (Milwaukee, WI), hexane (GC-MS/HPLC grade) and acetone (HPLC grade) from Fisher Scientific (Fairlawn, NJ), XAD-4 (2 section 400/200 mg), and Anasorb CSC charcoal (2 section 400/200 mg) sorbent tubes from SKC Inc. (Eighty Four, PA). A 1 mil (0.025 mm), clear, high-density polyethylene (HDPE) tarp was supplied by Dow Chemical Company (Midland, MI). The soil used was an Arlington series sandy loam soil (75% sand, 18% silt, 7% clay; 0.92% organic matter; pH 7.2) collected from the upper 20 cm of field 2B of the University of California–Riverside Agriculture Experimental Station. The gravimetric moisture content of the soil was 5%.

Biochar Preparation. The biochars used in this study were obtained from two types of waste biomass: rice husk and green waste. These are produced in large quantities by the agricultural and forestry industries and are therefore considered to be important source materials for biochar production. The rice husks were collected from a farm located in a suburb of Shanghai, China. After being dried at 105 °C for 48 h, the husks were ground (<3 mm) and placed into porcelain crucibles. Lids were placed on the crucibles to produce an oxygen-limited atmosphere within during heating. The husks were pyrolyzed by placing the crucibles in a temperature-programmable muffle furnace. The heating rate was set at 10 °C min^{-1} and increased to 400 °C, with a holding time of 5 h at the final temperature. The green waste was a mixture of plant prunings, mainly from the camphor tree (*Cinnamomum camphora*). It was biocharred at a temperature of around 400 °C in self-sustained carbonization equipment under an oxygen-limited condition, following the procedures reported by Idris et al.[24] The 400 °C charring temperature was chosen based on the recommendation of Brown et al.[25] for the manufacture of biochar for soil amendment purposes. The biochars derived from rice husk and green waste are referred to as BR and BG, respectively. As with our previous study,[26] the biochars were ground and passed through a 0.4 mm sieve before being used for characterization and soil experiments.

Characterization of Biochar. All characterization tests were performed in triplicate. The concentrations of C, H, N, and O in the biochars were determined using a CHNS/O Analyzer (PerkinElmer, 2400 II). The specific surface area (SSA) was measured by N_2 adsorption isotherms at 77 K using a Surface Area and Porosimetry Analyzer (Micromeritics Inc., USA). Scanning electron microscopy (SEM) was used to determine morphology of the biochars, and this was equipped with energy dispersive X-ray spectroscopy (EDX) for elemental analysis of the surface of the biochar samples. The surface organic functional groups were identified using Fourier Transform Infrared Spectroscopy (FTIR). The pH of the carbon surface was measured with a digital pH meter in deionized water using a 1:5 (w/w) ratio. Ash content was measured by heating the biochars at 900 °C for 2 h and then cooling at room temperature and calculating the difference between the mass of the biochars before and after baking.

Soil Column Experiments. The column system used in the study has been previously described in detail.[5,27,28] Briefly, duplicated cylindrical (12 cm diameter × 150 cm length) stainless steel soil columns were packed with the Arlington soil to a uniform dry bulk density of 1.50 g cm^{-3}. The columns were housed at 25 °C. For BR and BG soil column treatments, 34 g of biochar was mixed with 51 mL of water and applied to the soil surface as a slurry (equivalent to a 1% application to the top 20 cm of soil[17]). These treatments were compared to a fumigated bare soil (no emission reduction strategy), surface application of ATS, and soil surface tarping with HDPE. For the ATS treatment, 390 mg of ATS in 51 mL of water was sprayed to cover the soil surface (the same volume of water was also applied to the Bare and HDPE columns to mitigate any confounding influence of water). For the HDPE treatment, the tarp was applied over the soil surface and sealed to the top of the column using epoxy resin to produce a leak-free covering.

After establishment of the treatments, a stainless steel emission chamber was sealed onto the surface of the soil column and was swept with clean air at a rate of 100 mL min^{-1} to channel fumigants emitted from the soil surface through sorbent tubes (XAD-4 primary tube and charcoal backup tube, connected in series) which trapped the chemicals from the air stream. On day 0, 125 μL (178 mg) of Pic-Clor 60 was injected

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Table 1. Selected Physico-Chemical Properties of the Biochars Derived from Rice Hull (BR) and Green Waste (BG)

biochar	pH	N (%)	C (%)	H (%)	O (%)	ash (%)	molar H/C	molar C/N	molar O/C	SSA (m^2 g^{-1})[a]	APR (nm)[b]
BR	10.56	0.68	47.86	2.37	10.32	48.5	0.59	82.11	0.16	2.66	6.14
BG	8.73	1.82	54.26	3.01	23.3	53.3	0.67	34.78	0.32	6.18	2.49

[a]SSA: Specific surface area. [b]APR: Average pore radii.

into the soil through an injection port at 46 cm depth. This equated to a field application rate of 158 kg ha^{-1}, an intermediate application rate for Pic-Clor 60 based on the manufacturer's guidelines. Sorbent tubes were replaced every 4 h initially. After 224 h, when emissions were expected to be very low, the sampling interval was increased to 6 h. On a daily basis, vertical fumigant distribution within the soil pore space was determined by removing 250 μL of soil gas from a series of ports installed at 2, 5, 10, 20, 30, 40, 50, 60, 70, 90, 110, 130, and 150 cm below the soil surface. A gastight syringe was used to inject the sample into 12 mL glass vials that were immediately capped with a Teflon-faced butyl rubber septum and an aluminum crimp seal for analysis by headspace-gas chromatography. At the end of the experiment, 0.5 g samples of biochar were taken from the soil surface for extraction with 15 mL acetone to determine the amount of adsorbed fumigant. From preliminary experiments, the analytical recoveries of cis 1,3-D, trans 1,3-D and CP were 84, 83, and 71% for BR and 87, 87, and 80 for BG.

Analysis. XAD-4 and charcoal sorbent tubes were stored at −19 °C until extraction and analysis (a maximum of 4 weeks). The XAD-4 tubes were extracted by separating their two sections and placing each into a 20 mL glass vial. After the addition of 4 mL of hexane, the vials were immediately capped with a Teflon-faced butyl rubber septum and aluminum crimp seal, shaken for 1 h, and around 1.5 mL of supernatant solution transferred to a glass vial for analysis. The two sections of the XAD-4 tubes were extracted and analyzed separately. Charcoal tubes were extracted in the same way but using acetone rather than hexane; however, these contained nondetectable levels of the fumigants suggesting that breakthrough did not occur. Preliminary studies showed that the recoveries of cis 1,3-D, trans 1,3-D and CP from the XAD-4 tubes were 83, 78 and 87%, respectively, and that recoveries were not affected during 4 weeks of storage.

Analysis of biochar extracts and XAD-4 and charcoal tube extracts was carried out using an Agilent 7890A gas chromatograph (GC), equipped with a microelectron capture detector (Agilent Technologies, Wilmington, DE). Analytical conditions were as described by Ashworth et al.[5] and the limits of quantitation were 0.138, 0.139, and 0.0114 μg per tube for cis 1,3-D, trans 1,3-D and CP, respectively. For the soil gas samples, an Agilent 6890 GC equipped with a microelectron capture detector and an Agilent automated headspace sampler was used. Analytical conditions were as described by Ashworth et al.[28] and the limits of quantitation were 3.094×10^{-3}, 3.802×10^{-3} and 1.435×10^{-4} μg mL^{-1} for cis 1,3-D, trans 1,3-D and CP, respectively. For each analysis, 10 standards were prepared to encompass the range of values in the samples.

Microbial Respiration Analysis. After the column experiments, soil basal respiration was determined over 10 weeks using surface soil samples from the columns to provide a bench-scale measurement of CO_2 release. The CO_2 emission rates from soil often reflect the soil microbial activity.[29] The measurement of the CO_2 release from soil was carried out by a modified alkali absorption method.[30] For each of the BR, ATS, and HDPE columns, soil from the top 30 cm was removed from the column and mixed (including thorough mixing with the biochar where present). This would simulate a farmer plowing the biochar into the soil after a growing season. Plowing between cropping seasons is common practice for many of the typical crops requiring fumigation (e.g., fruits and vegetables). Next, 300−400 g (dry wt.) samples of soil were transferred into stainless steel chambers (12 × 4 cm). To investigate whether the mixing of biochar with fumigated soil aids recovery of the soil microbial population to its prefumigation level, we used nonfumigated soil as a control. The chambers were incubated at 25 °C (the same as the column studies). Each week, for 10 weeks, CO_2 release from the soil was measured. A Petri dish (5 × 1.5 cm) was placed on the soil surface and 10 mL of 1 M NaOH were added to the Petri dish. The system was completely sealed with a stainless steel cover and aluminum tape. Over the subsequent 48 h, released CO_2 was absorbed by the NaOH. The absorbed CO_2 was determined by titrating the excess NaOH from the Petri dish with 0.01 M HCl using phenolphthalein and methyl orange as indicators.

RESULTS AND DISCUSSION

Characteristics of Biochars. The selected physical and chemical properties of BR and BG biochars are shown in Table 1. Both biochars were alkaline, but BR had a higher pH than BG (10.56 vs 8.73, respectively). Abe et al.[31] indicated that cellulose and hemicelluloses could be decomposed around 200−300 °C, producing organic acids and phenolic substances that lowered the pH of the products. Beyond 300 °C, alkali salts begin to separate from the organic matrix and increase the pH of the product. After complete release of alkali salts from the pyrolytic structure, pH becomes constant.[32] The SEM-EDX analysis showed that BR was abundant in mineral elements, especially silicon (Si). Guo and Chen[33] also reported the formation of Si−C bonds in biochars derived from rice straw. Si−C is expected to be a suitable semiconductor for the dehalogenation of compounds, even those with low reducibility, because the conduction band of Si−C lies at high energy.[34] Therefore, the higher pH and mineral content of BR suggests that it has potential as a mediator to promote the catalytic hydrolysis of fumigants. The ash content of the BG biochar was greater than BR (53.3% for BG and 48.5% for BR). A high ash content and its interaction with organic moieties may influence the interaction of biochars with organic pollutants by reducing the accessibility of organic sorption sites. However, the influence of biochars of high ash content on the fate of soil fumigants is not yet fully understood.

Compared to BR, BG contained higher concentrations of C and H. This was likely the result of differences in both the feedstock and pyrolysis conditions used to produce the biochars. Demirbas[35] and Fuertes et al.[36] found that C content was higher in hardwood than in corn stover. The degree of carbonization may be described by the molar H/C ratio because H is primarily associated with plant organic matter. In comparison with activated carbon, which has typical H/C ratios

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of 0.12−0.26,[37,38] the observed H/C ratios of 0.59 and 0.67 for BR and BG, respectively, indicate that these biochars were weakly carbonized and likely still contained a certain amount of the original organic plant residues such as cellulose.[38] The SSA of BG was smaller than that of BR (2.66 vs 6.18 m^2 g^{-1}, respectively, Figure S1), whereas the average pore radii (APR) of BR could be classed as a mesopore (according to IUPAC) and was larger than that of BG (6.14 nm vs 2.49 nm). Therefore, the SSA was not proportional to the total pore volume, since the pore size distributions are different.[39]

Scanning electron spectroscopy images also revealed that mesopores were present in the biochar materials (Figure 1).

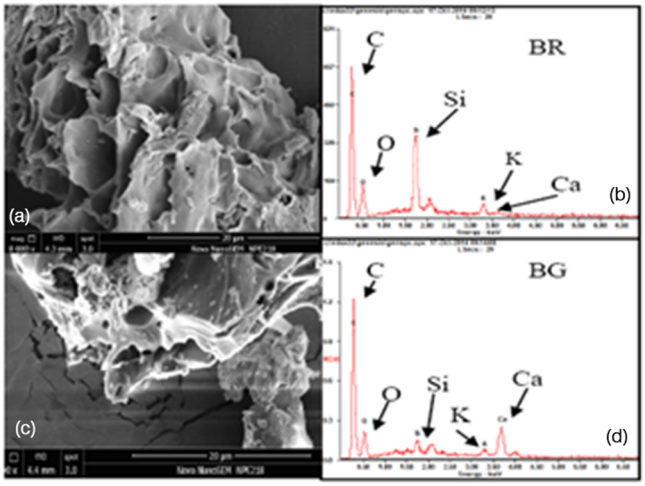

Figure 1. SEM images (left) and corresponding EDS spectra (right) of the BR (a and b) and BG (c and d) biochars. The EDS spectra were obtained at the same location as shown in the SEM images.

These pores are of importance to many liquid−solid adsorption processes.[40] With the existence of mesopores in carbon, the path length of the micropores that allow for diffusion from mesopores to the carbon interior will be shorter than that when the diffusion comes directly from the bulk phase to the interior without the aid of mesopores. Under this condition, mesopores may play a role in not only accelerating diffusion into micropores, but also in increasing the equilibrium coverage of the micropores.[39] The SEM images of BR and BG revealed that the biochar structures were not homogeneous and had irregular pores with different shapes and sizes. Given the differences in porosity, it would be expected that BR may be more effective at reducing fumigant emissions due to its greater potential for chemical adsorption within its more extensive pore structure.

The type and concentration of surface functional groups has been reported to play an important role in the adsorption capacity and the removal mechanism of adsorbates.[41] The FTIR spectra of the biochars revealed a broad band near 3400 cm^{-1} arising from the stretching vibration of hydroxyl groups and indicated significant hydrogen-bonding interactions (Figure 2). The sharp peak appearing at the wavenumber of 1433 cm^{-1} can be used to confirm the COO stretching vibration. The carboxyl that lost hydrogen ions became the COO−, which is related to the alkalinity of both biochars.[42,43] The stretching vibration of the C−H bond in aromatic structures is visible as a band at around 2924 cm^{-1}.[41] The bands at 1600 cm^{-1} were assigned to the C−C═C, C═O, and C−N of aromatic components, conjugated ketones, and quinones.[44,45] Quinone moieties are one of the key types of redox-active structure in

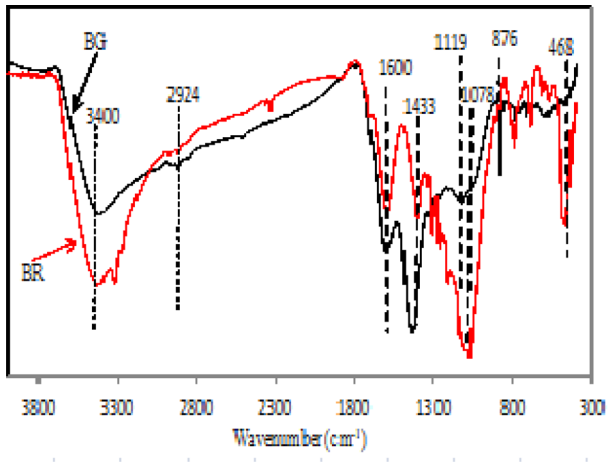

Figure 2. FTIR spectra of the BR and BG biochars.

the electron transfer catalysis of biochar.[46] The bands at 1119 and 1078 cm^{-1} were assigned to the aliphatic C−O and alcohol − OH, and were stronger in BR than BG. A band at 876 cm^{-1} was assigned to the γ−CH of furan,[47] and was observed only in BG. In contrast, the band near 468 cm^{-1}, which was assigned to aromatic C−H in BR, was stronger than those in BG. The FTIR results demonstrated qualitative differences in the surface functional groups of the two biochars that were likely due to differences in both the original feed stocks as well as differences in the pyrolysis conditions (Figure 2).

The BR biochar was a slow pyrolysis biochar, produced by pyrolyzing in an O_2-free atmosphere in a ceramic fiber muffle furnace. Although its pyrolysis temperature (around 400 °C) was close to that of BR, the BG was manufactured in carbonization equipment (i.e., kiln carbonization). Biochars from such a process are considered distinct from slow pyrolysis or gasification biochars because their process temperatures will be similar to slow pyrolysis, their reaction atmosphere oxygen contents will be similar to gasification, and their residence times will vary. Brewer et al.[48] proposed that the presence of oxygen used to drive the heat-generating combustion processes in commercial kilns creates unique biochars whose properties represent a combination of slow pyrolysis and gasification biochar properties.

Fumigant Emission Rates. The 1,3-D and CP emission fluxes of the fumigants from each column treatment are shown in Figure 3. With the exception of the biochar treatments, the fluxes increased rapidly following fumigant injection and then slowly decreased. For the bare soil (no emission reduction strategy), the peak emission flux was higher and reached more rapidly (at around 16 h) for both 1,3-D (13.1 μg $m^2 s^{-1}$) and CP (9.5 μg $m^2 s^{-1}$) than in any of the other treatments. The peak emissions in the HDPE treatment were 6.7 μg $m^2 s^{-1}$ for 1,3-D and 1.9 μg $m^2 s^{-1}$ for CP; whereas in the ATS treatment, the values were 5.2 and 1.9 μg m^2 s^{-1}, respectively. Emission fluxes of CP were lower and occurred over shorter time periods than for 1,3-D due to the shorter half-life and lower vapor pressure of CP, even though its application rate was higher than that of 1,3-D (106.6 and 71.4 mg of CP and 1,3-D, respectively). These results are in agreement with those previously published[5] and indicate that fumigant emissions are likely to be highest in the absence of an emission reduction strategy. For 1,3-D, amendment of both BR and BG resulted in large decreases in emissions and no obvious single emission

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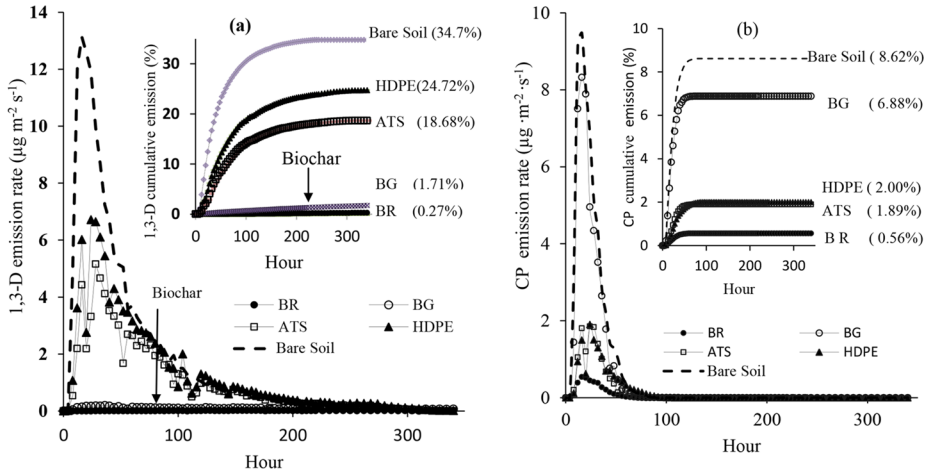

Figure 3. Emission rates and (insets) cumulative emissions of (a) 1,3-D and (b) chloropicrin. The values are an average of the two measurements.

peak when compared to the other treatments (Figure 3a). The emission fluxes were below 0.02 μg m^{-2}s^{-1} for BR and 0.19 μg m^{-2}s^{-1} for BG. The peak emission flux in the BR treatment was reduced by 99.6% as compared to the bare soil, by 99.1% compared to the ATS treatment, and by 99.3% compared to the HDPE treatment. In the BG treatment, the peak emission flux was reduced by 96.5% from that of the bare soil, 91.4% from that of the ATS treatment, and 93.5% from that of the HDPE treatment. The decreasing order of the emission flux maxima for 1,3-D was: Bare Soil > HDPE > ATS > BG > BR. For CP, the peak emission flux in the BR treatment was reduced by 89.4% from that of the bare soil, 72.2% from that of the HDPE treatment, and 70.6% from that of the ATS treatment. In the BG treatment, however, the peak CP emission rate was only reduced by 36.2% from that of the bare soil and was greater than those of the HDPE and ATS treatments by 66.7 and 76.5%, respectively. The decreasing order of the CP emission fluxes was: Bare Soil > BG > HDPE > ATS > BR (Figure 3b). It is not clear why the BG biochar did not reduce CP emissions as effectively as it did for 1,3-D, or as effectively as the BR biochar. We may postulate that adsorption sites on the BR biochar were not as effective for CP as they were for 1,3-D (perhaps competitive adsorption favored 1,3-D), whereas this was not an issue for the BR biochar.

Overall, BR amendment to the soil surface was the most effective of the treatments at reducing emission rates compared to a bare soil treatment. Indeed, the maximum emission fluxes were comparable to those measured by Ashworth et al.[5] for virtually impermeable film (VIF) using the same column system (maximum emission rates of 0.37 μg m^2 s^{-1} for 1,3-D and 0.001 μg m^2 s^{-1} for CP). Because VIF is generally considered the most effective fumigant emission reduction strategy, this finding suggests that certain types of biochar may offer significant potential for protecting air quality following soil fumigation.

Cumulative Fumigant Emissions. Cumulative 1,3-D and CP emissions, expressed as a percentage of the total amount added, over the course of the experiment are shown in Figure 3a,b (insets) for 1,3-D and CP, respectively. These figures show that all treatments reduced emissions to various extents compared to the bare soil. Over the 2 week period, the cumulative emissions of 1, 3-D and CP were, respectively, 34.8 and 8.6% for the bare soil, 24.7 and 2.0% for the HDPE treatment, 18.7 and 1.9% for the ATS treatment, 1.7 and 6.9% for the BG treatment, and 0.27 and 0.56% for the BR treatment. The total emission reduction results showed that BR was the most effective strategy. This may relate to the higher ability of this biochar to adsorb, and perhaps degrade, the fumigants. Graber et al.[22] reported that sorption of 1,3-D on corn straw biochar (fast pyrolysis at 500 °C; SSA of 3.0 m^2 g^{-1}) was strongly nonlinear and they found significantly greater sorption on a soil−1% biochar mixture than on soil alone.

The adsorbed amounts of 1,3-D and CP on the biochar were determined after the experiment. As a percentage of 1,3-D amount added, the BR biochar adsorbed 27.3% and the BG biochar 18.2%, indicating that the biochars were a significant sink for the added 1,3-D. No CP was detected on either biochar at the end of the experiment. However, the emission flux data indicate that both biochars, but particularly BR, limited the release of CP to the air when compared to the bare soil, which strongly suggests that they did adsorb CP. This presents the likelihood that adsorbed CP was degraded by the biochar. Both 1,3-D and CP are chlorinated aliphatic compounds. Biochar-mediated transformation of pesticides has been explored in recent studies, and it has been suggested that the complex structure of biochar may offer both sorption sites and electron conductors. The latter may catalyze the reduction of some organic compounds, e.g., nitroaromatic compounds, thereby enhancing their degradation.[49] It was suggested that the ash constituents, including the alkalinity, released dissolved metal ions, and that the mineral surface played a catalytic role. Overall, the process of adsorption very likely explains the low level of emissions when either biochar was applied to the columns.

Fumigant Soil Gas-Phase Distribution. Consideration of fumigant gas concentrations in soil is essential for assessing the effect of emission reduction strategies on pest control efficacy. The distribution of 1,3-D and CP in the soil-gas phase over time is shown in Figure S1 (Supporting Information). Overall, gas concentrations decreased over time and differed across the treatments, agreeing with previous reports.[28] In the BG treatment, the peak in soil concentration occurred at a soil depth of 50−60 cm, which was the same as for the bare soil, ATS, and HDPE treatments. However, the peak concentration occurred at 30 cm in the BR treatment, suggesting that enhanced adsorption on the biochar at the soil surface significantly affected, via diffusive processes, 1,3-D and CP distributions within the upper soil (root zone). However,

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although the biochar amendments yielded lower gas concentrations than under HDPE at the first sampling time, these were similar to concentrations in the ATS treatment (~3.0 μg mL^{-1} for total 1,3-D plus CP in the biochar treatments, and ~3.4 μg mL^{-1} in the ATS treatment). As Gan et al.[27] indicated that ATS showed no likely negative impact on fumigation efficacy, this result suggests that biochar amendment to the soil surface may also not result in reduced fumigation efficacy.

Effect of Biochar on Soil Respiration in Fumigated Soil. The recovery of microorganisms in fumigated soil can be gauged by soil respiration, with CO_2 efflux an index of total soil biological activity.[50] Soil respiration reflects the capacity of soil to support soil life including crops, soil animals, and microorganisms. Soil basal respiration is defined as the steady rate of respiration in soil and is estimated either on the basis of CO_2 evolution or O_2 uptake.[51] The measurement of soil basal respiration has been applied across a variety of studies and is commonly accepted as a key indicator for measuring changes in soil quality.[52] Basal respiration reflects the overall activity of the microbial pool.[53] To investigate whether the mixing of biochar with fumigated soil aids recovery of the soil microbial population to its prefumigation level, we used nonfumigated soil as a control. The BR biochar was compared with the control and the established emission reduction methods of ATS application and HDPE covering. Figure 4 shows the effect of

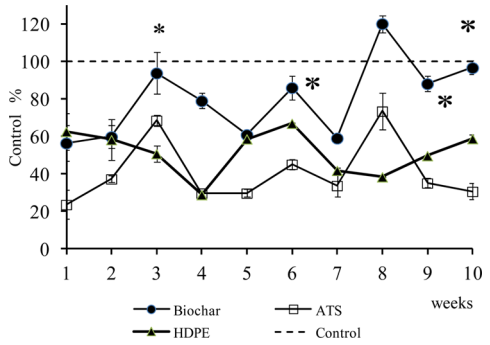

Figure 4. Microbial respiration (CO_2 production) over time for soil taken from the top 30 cm of selected soil columns, expressed as a percentage of that in a control (nonfumigated) soil. For the BR treatment, the biochar was mixed into the soil. Results are expressed as percent of control. The error bars indicate the standard deviation of the mean, and asterisks (*) indicate no significant difference (i.e., $p > 0.05$) compared to the control (determined by Analysis of Variance at weeks 8, 9, and 10).

BR biochar on soil basal respiration during the recovery of microorganisms in the fumigated soil. At 1 week, the soil basal respiration rates were 8.7, 3.6, and 9.6 mg CO_2 kg^{-1} dry soil 24h^{-1} for BR biochar, ATS and HDPE, respectively. As a percentage of the rate for nonfumigated soil, these were 56.3, 23.5, and 62.5%, respectively. Therefore, the activity of soil microorganisms was lowest in the ATS treatment. This may have been due to the particular degradation products of the ATS-mediated degradation (dehalogenation) of 1,3-D and CP, which perhaps influenced the soil microorganism recovery.[54] Soil basal respiration in the BR treatment increased over time. At the eighth week, the BR soil respiration exceeded the control (nonfumigated) soil. Soil basal respiration was 17.1 mg CO_2 kg^{-1} dry soil 24 h^{-1}, which was 119% of the nonfumigated soil and indicates complete, and relatively rapid, recovery of the microbial population. In contrast, soil basal respiration was 23.5−68.4% and 28.8−66.8% of the nonfumigated soil in the ATS and HDPE treatments, respectively, throughout the experiment. Therefore, compared with the HDPE and ATS treatments, mixing of biochar into the soil markedly enhanced the recovery rate of soil microorganisms after fumigation. Many researchers have shown that mixing of biochar into soil frequently appears to stimulate the microbial population and activate dormant soil microorganisms.[55] The activation of dormant soil microorganisms may explain the observation that respiration in the BR treatment actually exceeded the nonfumigated soil. Further studies should be conducted to evaluate the effect of biochar on the recovery of microorganisms in different fumigated soils at different rates of biochar application.

Overall, in this study, we reported a method of applying biochar to the soil surface for reducing fumigant emissions. The biochar was applied as a liquid slurry that would aid the prevention of wind losses under field conditions. Our results suggest that biochar amendment to the soil surface is not only a potentially highly effective strategy for fumigant emission reduction but may also maintain soil gas concentrations for pest kill efficacy and speed up the recovery of the soil microorganism population established postapplication after the biochar is mixed into the fumigated soil. The emission reduction effect was dependent on the original feedstock of the biochar and its surface characteristics. In the present study, compared to BG biochar, HDPE, and ATS, the BR biochar (produced at a pyrolysis temperature of 400 °C) gave the greatest emission reductions for 1,3-D and CP, and had no obvious single emission peak. The degree of BR emission reduction was comparable to that observed for VIF (generally considered the most effective means of emission reduction) in previous studies. This effect may be related to the physicochemical properties and surface functional groups of the biochar, such as its alkalinity, mesopore structure, Si mineral elements, and quinone moieties, which likely promoted adsorption of the fumigants. Analysis of the amount of fumigant residue on the biochar at the end of the column experiment showed that BR and BG at the soil surface trapped 27.3 and 18.2% of the initially applied 1,3-D, respectively, whereas CP was not detected on either biochar. It is possible that the CP, and some of the adsorbed 1,3-D, underwent degradation catalyzed by the biochar. Further research should be conducted to understand biochar-induced degradation or inactivation of these and other fumigants. In the future, it would also be worth comparing the use of raw (prebiochar) materials with biochar in terms of fumigant reduction. By comparing biochars with the raw material from which they were produced, we could determine the effect of the biocharring process on emissions. Moreover, the effect of biochar feedstock, pyrolysis conditions, and particle size on reducing fumigant emissions should be evaluated.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b03958.

SSA desorption isotherms for the two biochars used in the study, together with soil gas distributions of 1,3-D and CP over the course of the experiment. (PDF)

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Notes

The authors declare no competing financial interest.

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