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Effects of field-aging on the impact of biochar on herbicide fate and microbial community structure in the soil environment

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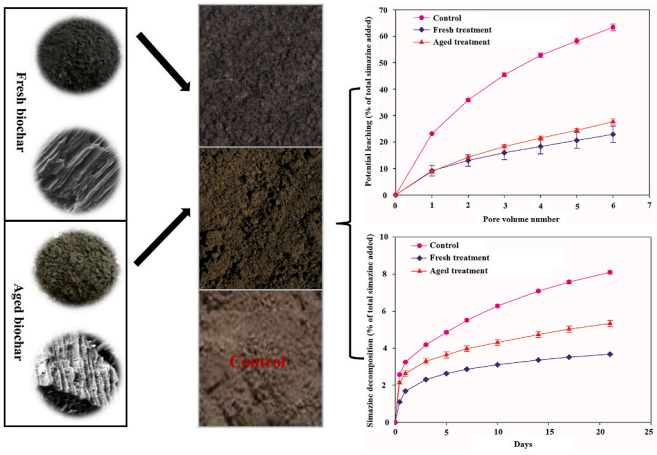
HIGHLIGHTS

- The treatment performance of aged and fresh biochar in pesticide-polluted soil was evaluated.
- Field-aging lowered the biochar adsorption capacity for simazine in the soil environment.
- Fresh biochar increased arbuscular mycorrhizal fungi but reduced eukaryotes in the soil environment.
- Fresh biochar significantly lessened the leaching and decomposition of simazine in the soil.

GRAPHICAL ABSTRACT



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ABSTRACT

Biochar can enhance organic carbon storage and mitigate the adverse effects of pesticides in the soil. However, the mechanisms by which field-aging affects the impacts of biochar on herbicide behavior and the composition of microbial communities in the soil remain unclear. This study aimed to investigate the influences of aged and fresh biochar on herbicide behavior and microbial community structure in the soil. Herein, with ^{14}C-labeled

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Adsorption
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Microbial diversity

technology, aged treatment (soil amended with field-aged biochar), fresh treatment (soil amended with fresh biochar), and control (soil without biochar) were installed to evaluate their treatment capacities. The results showed that the average leaching out and mineralization of simazine in the aged treatment were significantly higher by 4.8% and 1.66% ($P < 0.05$) compared with the fresh treatment. Relative to the control, the pesticide was significantly adsorbed ($P < 0.05$) in the aged treatment. The abundance of arbuscular mycorrhizal fungi (AMF) significantly increased by 1.03 and 1.16-fold, whereas fungi increased dramatically by 1.02-fold and decreased by 1.21-fold in the aged and fresh treatments, respectively ($P < 0.05$). In addition, eukaryotes were effectively reduced by 1.02 and 1.14-fold in these treatments, respectively ($P < 0.05$). This study suggests that field aging can undermine the impacts of biochar on pesticides and modify the microbial community structure in the soil environment.

1. Introduction

The extensive and inefficient use of pesticides in agriculture has significantly contaminated soils, crops, and water sources (Hassaan and El Nemr, 2020; Onwona-Kwakye et al., 2020), threatening human and animal health. Prolonged exposure to pesticides is commonly associated with health problems, including liver, colon, lung, and prostate cancer (Sharma et al., 2020). It is also linked with other disorders in different body parts such as the eyes, central nervous, digestive, and reproductive systems. According to multiple surveys, every year, 1 in 5000 individuals working in agriculture suffers from pesticide poisoning, while 200,000 people lose their lives due to high exposure to these substances (Faber, 2020). Alternatively, the use of pesticides in agricultural soils leads to fluctuations in their physicochemical properties (Al-Ahmadi, 2019; Karpouzas et al., 2016). Pesticides harm the microorganisms and enzymes in the soil due to their xenobiotic properties (Arora et al., 2019; Micuti et al., 2018).

Nonetheless, these microorganisms and enzymes are vital indicators of a soil's ability to tolerate pollution. Triazine herbicides, like atrazine and simazine, are widely used pesticides in crop fields. Their residues can remain in the soil for extended periods (Galon et al., 2021), increasing the risk of them seeping into other environmental compartments (Galon et al., 2021), such as surface and groundwater. This poses a significant threat to aquatic life, leading to the death of fish and other organisms. To date, high quantities of herbicide residues are often detected in the soil and water (De Souza et al., 2020; Vryzas, 2018). Therefore, it is crucial to prioritize and give considerable attention to identifying the most appropriate and practical environmental remediation approach for controlling the dispersal of pesticides in the environment.

Various studies have been conducted to investigate the potential of different approaches like amendment of dead leaves, rice husk, tree bark, fruit peel, and biochar in transforming or immobilizing pesticides and other pollutants in the soil (Kumar et al., 2023; Kwon et al., 2022; Yang et al., 2023). Among the amendments mentioned above, biochar has attracted significant attention in the last two decades. This is because immobilization, degradation, and reduction of pollutants and their risk in the soil with this method are seen as ecologically friendly and commercially feasible (Niazi et al., 2018). It enhances crop productivity by improving soil quality, reducing greenhouse gas emissions, and decreasing the amount of fertilizer and water that are needed in the field (Niazi et al., 2018; Nie et al., 2018).

Biochar possesses a substantial surface area, remarkable stability, and a high adsorption capacity. When it is added to the soil, it can significantly diminish the leaching and biodegradation of pesticides (He et al., 2019), thereby improving soil fertility and crop yield. It also enhances the chemical and physical properties of the soil, enabling it to better retain pesticides. This reduces the chances of pesticides being leached and biodegraded by natural processes (Cheng et al., 2017; Williams et al., 2015), decreasing their harmful environmental effects. The amount of pesticides in soil that is regulated depends on biochar pyrolysis temperature, feedstock, and holding time (Cheng et al., 2018; Itoh et al., 2020; Pariyar et al., 2020), and several studies have confirmed it (Ali et al., 2019). Most of the studies have been conducted using fresh biochar, while a few studies have explored the effects of field aging on the impacts of biochar in the soil, resulting in limited knowledge about how herbicides behave in the soil. Hence, it is vital to assess the effects of field aging on the influence of biochar on the behavior of herbicides in the soil environment.

Typically, the characteristics of biochar change over time due to weathering or aging processes (Gámiz et al., 2019). The aging process of biochar significantly occurs when it is buried in the soil for an extended period (Wang et al., 2020). This process is regulated by living (biotic) and non-living (abiotic) parts of an ecosystem, such as microbial activity, crop types, tillage practices, exposure to UV radiation, moisture levels, and fluctuations in temperature (Sorrenti et al., 2016). As biochar ages, its pores get clogged by mineral particles, roots, organic matter, or microorganisms, reducing the surface for chemical reactions (Ren et al., 2018b). This definitely affects its influence on pesticides in the soil. However, the mechanisms of how biochar properties change during aging and how these changes influence the behavior of herbicides have not been adequately explored, which restricts their potential use in soil remediation.

The objectives of this study were to investigate the effects of field aging on the impact of biochar on herbicide fate and to elucidate how biochar influences the structure and community of microorganisms in the soil environment. The microbial community structure and abundance profile were quantified using phospholipid fatty acid (PLFA) analysis. The functional groups in treatments were assessed using fourier transform infrared radiation spectroscopy (FTIR).

2. Materials and methods

2.1. Materials and chemical reagents

Sandy clay loam soil was gathered on a 0–15 cm topsoil surface in a temperate maritime climate zone (Abergwyngregyn, Wales, UK) with 1066 mm of rainfall and a mean annual temperature of 10 °C. The collected soil sample was dried by air exposure, sieved through a 2 mm mesh to remove any stones or roots, and stored at room temperature for physicochemical analyses. The properties of the soil used in this study are given in Table S1.

Biochar was bought from Bioregional Charcoal Company at Abergwyngregyn, Wales, UK (53°14′N, 4°01′W) (Jones et al., 2012). Since 2009, that company has produced biochar from Quercus robur L., Fagus sylvatica L., and Fraxinus excelsior L. at 450 °C for 48 h. Then, the purchased biochar was tightly sealed for 9 years and labeled "fresh biochar." On the other hand, field-aged biochar was obtained from a field trial conducted in September 2018 and prepared in the following manner: The soil and biochar mixture that had been reserved during the field trials was collected and sent to the laboratory. It was then naturally dried to an appropriate level. Next, the biochar was separated from the soil by hand and visual inspection. Any soil that remained attached to the biochar was washed away through small holes with a diameter of less than 0.5 mm. The biochar was then further separated from mud or gravel based on density. To prevent the biochar from being discarded as waste, any solid material at the bottom was carefully removed using a brush. Finally, any remaining crumbs still mixed with the biochar were

manually picked out. Table 1 presents the physicochemical properties of fresh and aged biochar used in the experiments.

All chemical reagents were purchased from Sigma-Aldrich Chemical Reagent Company Ltd. (UK). All reagents and solvents were not further purified before being used. Simazine (^{14}C-Labeled Simazine) was used in the decomposition, adsorption, and leaching experiments. Sodium hydroxide (NaOH) was used in the decomposition experiment to capture the $^{14}CO_2$ produced. Calcium chloride ($CaCl_2$) was used in the adsorption experiment as a base solution. Potassium sulfate (K_2SO_4) was used to extract nitrate nitrogen, ammonia nitrogen, and dissolved organic carbon from the soil. Ammonium acetate ($C_2H_4O_2{\cdot}H_3N$) was used to measure potassium content and as a soil extract to measure biochar's cation exchange capacity (CEC). Potassium sulfate (K_2SO_4) was used to extract biochar for measurement. The methanol-chloroform-phosphate buffer solution was used in the phospholipid fatty acid (PLFA) analysis to extract PLFA from the soil. Saponification and methylation reagents were used in the PLFA analysis to separate and obtain PLFA.

2.2. Experimental setup

This study consisted of three equally sized parallel rectangular plastic boxes (12.2 cm × 8 cm × 10.5 cm), which are (1) the control treatment, which consisted of soil without the addition of biochar; (2) the aged treatment, which consisted of a mixture of field-aged biochar and soil; and (3) the fresh treatment, which consisted of a mixture of fresh biochar and soil. The mixture of biochar and soil was homogenized by hand at 1:25 for each treatment. This rate was estimated to compensate for the uneven distribution of biochar in the field, where 40 tons are sprinkled for one ha in the 0–10 cm surface layer. The homogenized sample (*300* g) was separately placed into a polypropylene container and watered with distilled water to maintain the soil's *70%* water-holding capacity. All containers were stored in the dark at *10* °C for *14* d to allow microbial recovery (Jones et al., 2011) and then transferred to *20* °C for *30* d. Afterward, samples were taken from each treatment for different analyses. Specifically, 10.0 g was taken for PLFA analysis, 6.5 g was taken for decomposition experiments, another 6.5 g was taken for leaching experiments, and finally, 2.6 g was taken for an adsorption experiment.

2.2.1. Decomposition experiment

6.5 g of soil was put into a 50 mL centrifuge tube during this experiment. Then, 0.5 mL of ^{14}C-Labeled Simazine (0.60 mg L^{-1} and 0.54 kBq mL^{-1}) was added to the tube and sealed. A trap containing 1 M NaOH was suspended above the treatment surface to capture any $^{14}CO_2$ that was produced. The traps were replaced on days 1, 3, 5, 7, 10, 14, 17, and 21. The activity of $^{14}CO_2$ in the NaOH traps was determined using the method described by Cheng et al. (2021).

2.2.2. Adsorption experiment

Adsorption experiments were carried out to obtain simazine adsorption isotherms at different concentrations. In these experiments, the incubated 2.6 g of soil (eq dry soil, *2.0* g) was weighed into a 50 mL centrifuge tube. To prevent the breakdown of simazine by microorganisms, the tubes were heated at 80 °C for 30 min (Kuzyakov and Jones, 2006). Then, different amounts of ^{14}C-labeled simazine (6.25, 12.5, 25, 50, and 100 μg l^{-1}; 20 ml; 0.05 kBq ml^{-1}) were put into tubes with a 0.01 M $CaCl_2$ base solution. The tubes were then shaken for 24 h at 20 °C (200 rev min^{-1}). After centrifugation (*3850 g*, 10 min), 1 ml of the solution was extracted to assess the amount of ^{14}C-simazine in the supernatant. The distribution coefficient (K_d) and isothermal adsorption curves were then calculated.

2.2.3. Leaching experiment

Based upon a previous study conducted by Cheng et al. (2017), 6.5 g of incubated soil (eq dry soil 5 g) was taken and placed into an inverted syringe (25 mL) with a polypropylene mesh (1 mm) at the bottom to minimize soil loss during the experiment.

Afterward, 1 ml of ^{14}C-labeled simazine (0.05 kBq ml^{-1}, 2.50 mg l^{-1}) was evenly sprinkled on the top layer of the soil. The syringe was then placed on the laboratory bench for 1 h to allow the simazine to reach equilibrium. A polypropylene mesh (1 mm) was covered on the soil. Distilled water was sprayed onto the soil using a syringe pump at 0.2 mL min^{-1}. The resultant leachate was collected in a specific sequence corresponding to 1, 2, 3, 4, 5, and 6 soil pore volumes, and its ^{14}C activity was then assessed using the previously described method.

2.3. Determination methods

2.3.1. Physical and chemical properties analysis

The tests were performed four times on each sample. Soil measurement was obtained by mixing a dry soil sample and distilled water (1/2.5, w/v), whereas biochar measurement was obtained by blending biochar and distilled water (1/5, w/v). EC and pH were determined using standard probes for pH (PHS-3 C, Leici, Shanghai) and EC (DDS-307, Leici, Shanghai). According to the colorimetric methods of Miranda et al. (2001) and Mulvaney. (1996), nitrate nitrogen and ammonia nitrogen were determined with 0.5 M K_2SO_4 (1/5, w/v) extract. K_2SO_4 extract was also used to measure soil-dissolved organic carbon (DOC). Total carbon (C) and nitrogen (N) in the solid phase were measured using a Trustees® C/N analyzer (Leco Corp, St Joseph, MI). Potassium (K) was measured with 1 M ammonium acetate soil extracts (1:5 w/v) using flame photometry (Helmke and Sparks, 1996). Biochar ash content was calculated based on the weight loss of biochar after its combustion at 575 °C for 16 h. The vario macro cube analyzer determined the relative amounts of C, N, H, and S. The O content was calculated by accounting for the ash content and using the assumed quantities of C, N, H, and O that constituted biochar (Zimmerman, 2010). The modified ammonium acetate method was used to determine the CEC of biochar (Gaskin et al., 2008). The water-holding capacity (WHC) of the biochar was measured based on the guidelines set by the EBC (2012). The specific surface area (SSA) of the biochar was assessed using an Autosorb iQ/monosorb surface area analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). The ^{14}C-specific activity in the traps was determined based on the method of Jones et al. (2011). Fourier transform infrared radiation spectra were assessed within the range of 4000–400 cm^{-1} of wavenumber using an infrared Raman spectrometer (VERTEX70, Germany). A malvern zeta meter (Nano ZSE + MPT2, Malvern Panalytical Instruments Ltd., UK) was used to evaluate Zeta potential. The surface morphology of biochar was examined using a scanning electron microscope (JSM 6460 LV; JEOL, Tokyo, Japan).

2.3.2. Determination of phospholipid fatty acid

PLFA analysis was assessed based on the method of Zang et al. (2020) and Cheng et al. (2016). 10 g of the cultivated sample was collected and then stored at −80 °C for PLFA profiling before freeze-drying. After that, 2.0 g of freeze-dried soil was mixed with a methanol-chloroform-phosphate buffer solution. The mixture was then sonicated for 10 min at 20 °C. After that, the sonication machine was turned off for 2 h, and then the sample was taken to be centrifuged for 10 min. Finally, the sample was filtered using 0.22 μm filter paper, followed by the chloroform phase.

Table 1
Physicochemical properties of fresh and aged biochar. All values presented are mean and standard deviations (n = 4).

Parameters	Aged biochar	Fresh biochar
pH	7.65 ± 0.49^b	9.61 ± 0.47^a
EC (μS/cm)	122 ± 10^b	1381 ± 21^a
CEC (cmol/kg)	24.3 ± 1.6^b	43.5 ± 6.4^a
SSA (m^2/g)	38.2 ± 0.5^b	46.0 ± 0.4^a
WHC (%)	187 ± 5^a	166 ± 5^a
Zeta potential (mV)	-40.7 ± 0.8^a	-38.6 ± 1.0^a

After that, solid-phase extraction was used to separate phospholipids from glycolipids and neutral lipids. After saponification and methylation, PLFA was obtained using a model 6890 gas chromatograph (Agilent Technologies, Wilmington, DE, USA). Several taxonomic groups were classified using the method of Frostegård et al. (1993). The caveats were obtained based on the technique of Frostegard A. Tunlid A. (2011). 70 fatty acids were observed in the sample, and more than 0.5% of PLFAs were chosen for biomarker and taxonomic class annotation.

2.3.3. Data calculation and fitting

The distribution coefficient (Kd) of simazine between a solution and soil was calculated using Eq. (1).

$$K_d = C_{solid}/C_{solution} \quad (1)$$

Where C_{solid} is the simazine concentration absorbed by the soil (μg g^{-1}), and $C_{solution}$ is the simazine concentration in the solution (μg L^{-1}). The langmuir and freundlich models were used to analyze the adsorption curves. The langmuir model was expressed using Eq. (2) in linear form, whereas the freundlich isothermal model was described using Eq. (3).

$$\frac{C_e}{q_e} = \frac{1}{q_{max} K_L} + \frac{C_e}{q_{max}} \quad (2)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (3)$$

Where q_e is the equilibrium adsorption capacity (μg g^{-1}), q_{max} is the maximum adsorption capacity (μg g^{-1}), K_L is the Langmuir constant related to the affinity of the binding sites, Ce is the equilibrium adsorbate concentration in an aqueous phase (μg L^{-1}), the constant K_F represents the adsorption capacity, and the constant n represents the adsorption intensity.

2.4. Statistical analysis

Variables were initially assessed for normality and homogeneity of variance. A one-way analysis of variance (ANOVA) was used to analyze normative variables. Variables with equal variances were analyzed using the fisher's least significant difference (LSD) method. A wilcoxon paired signed-rank test was used to analyze non-parametric variables with non-normal distributions or unequal variance (decomposition and leaching). Significant differences among the treatments were analyzed using an independent sample *t*-test in SPSS version 26.0 at a significance level of $P < 0.05$. Origin 2019b.0 (Origin Lab Corp., Northampton, MA) was used for linear regression analysis.

3. Results and discussion

3.1. Influences of aging on biochar characterization

As represented in Table 1, pH values significantly decreased after 9 years, from 9.61 (fresh biochar) to 7.65 (aged biochar). CEC decreased from 43.47 cmol kg^{-1} (fresh biochar) to 24.33 cmol kg^{-1} (aged biochar). Zeta potential increased from −38.58 mV (fresh biochar) to −40.69 mV (aged biochar). This indicates that biochar undergoes chemical, physical, and biotic changes once introduced into the soil (Rechberger et al., 2017; Ren et al., 2018a). Most studies on artificially simulated aging have shown that aging or modification processes remove volatile organic compounds (VOCs) from biochar, thereby increasing its specific surface area (SSA) (Shi et al., 2015; Vithanage et al., 2015). In contrast, other studies have reported that aging decreases SSA by destroying the structural integrity of the biochar (Wang et al., 2018). After 9 years of natural aging, the SSA decreased from 46.04 m^2 g^{-1} to 38.2 m^2 g^{-1}, visually supported by the surface morphology measurements. As depicted in Fig. S1, the image of the fresh biochar surface is smooth, with no particles visible in the pores. Contrarily, the surface of aged biochar is significantly rough due to the pores filled with tiny particles. This could also be the main reason for the decrease in SSA.

As shown in Fig. S2a, there is a significant difference ($P < 0.05$) between the atomic ratios of aged and fresh biochar. Compared to aged biochar, the nitrogen and oxygen-to-carbon ratios in fresh biochar were significantly higher by 1.8 and 1.86 times, respectively ($P < 0.05$). In contrast, the hydrogen-to-carbon ratio in aged biochar was markedly higher by 1.12 times compared with fresh biochar ($P < 0.05$). This confirmed that aging processes could significantly change the physical and chemical characteristics of biochar. As indicated in Fig. S2b, the carbon content of the fresh biochar was 56.68% and then increased by 17.78% after aging. This shows that the carbon content of biochar can be significantly enhanced through aging. Typically, biochar is taken as a remarkably stable form of carbon due to its highly aromatic structural composition (Lehmann et al., 2006). However, several studies have shown that biochar is slowly being oxidized in the soil, resulting in a change in the elemental composition of biochar as it ages (Dong et al., 2017; Ren et al., 2018a). The oxygen levels in fresh and aged biochar decreased from 22.1% to 14.5%, whereas the carbon content increased from 56.7% to 74.50% (Fig. S2b).

3.2. Effect of field aging on simazine adsorption and leaching

Based on the data shown in Fig. 1, the simazine absorption was significantly higher ($P < 0.05$) in the treatments with biochar than in the control treatment. At low concentrations (6.25 and 12.5 μg l^{-1}), the adsorption capacity of soil amended with fresh biochar was slightly higher compared to soil amended with aged biochar ($P < 0.05$). In general, the biochar treatments had a significantly higher solid phase-to-soil solution partition coefficient (K_d) (0.022 ± 0.001) compared to the control treatment (0.007 ± 0.000). Table S2 represents the parameters used to calculate the Freundlich and Langmuir isotherm models. As indicated in Fig. 2, the control group had an average leaching of simazine of 63.4 ± 1.3%. In comparison, the average leaching of simazine in aged and fresh biochar was 27.7 ± 1.1% and 22.9 ± 3.2%, respectively ($P < 0.05$). This is corroborated by previous studies that have also shown that adding biochar to the soil increased pesticide adsorption, thereby decreasing pesticide content in the leachate (Cheng et al., 2017; Khalid et al., 2020).

Experiments on simazine absorption and leaching showed that biochar improved the soil at absorbing simazine, which decreased the amount of simazine in the leachate. However, aging could reduce the

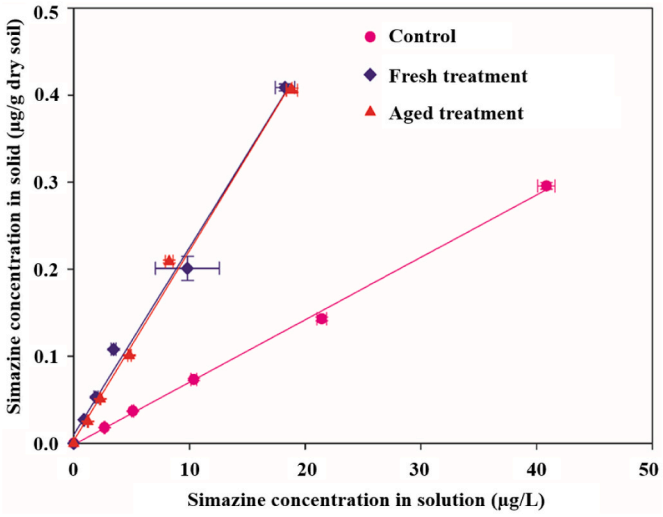

Fig. 1. Effect of fresh and aged biochar on simazine sorption to the solid phase in the soil. All values presented are mean and standard deviations (n = 4).

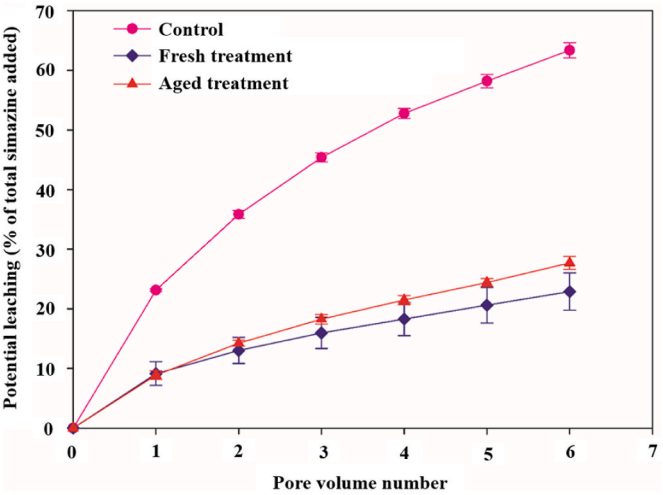

Fig. 2. Effect of fresh and aged biochar on potential simazine leaching in the soil. One pore volume leached is equivalent to the volume of the water-filled pore space in the soil. All values presented are mean and standard deviations (n = 4).

capacity of biochar to hold simazine in the soil. This may be because biochar aging significantly modified the properties of biochar (Mia et al., 2017a), reducing its adsorption capacity in the soil environment (He et al., 2019). This is consistent with the previous study demonstrating that aging could effectively alter biochar's elemental concentration and surface area (Ren et al., 2018b). The changes in biochar properties demonstrated that the adsorption of simazine to the biochar was slightly reduced after nine years of field aging (Table 1). This is linked to the adsorption and leaching experiment results (Figs. 2 and 3). Such results prove that biochar aging may decrease the adsorption of simazine in agricultural soils, which leads to more simazine dissipation in surface and groundwater.

Even though it has been shown that adding biochar to the soil could limit the amount of simazine absorbed by roots and its toxicity in the food chain (Yu et al., 2009), field aging could reduce its effectiveness. Therefore, the world population needs to pay more attention to biochar before it is used in the soil.

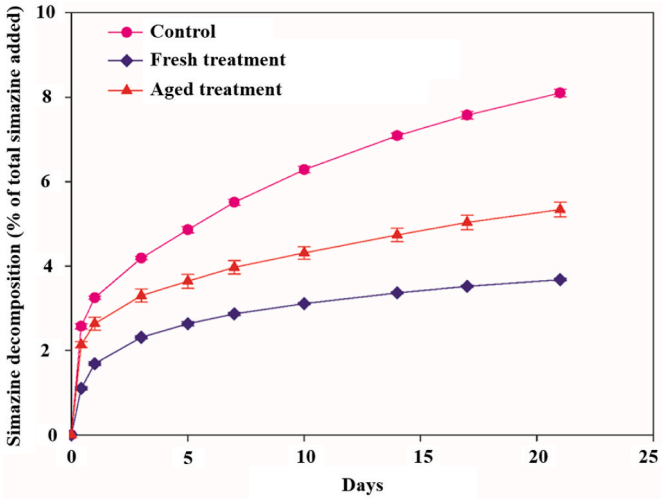

Fig. 3. Effect of fresh and field-aged biochar on simazine decomposition in the soil. All values presented are mean and standard deviations (n = 4).

3.3. Effect of field aging on simazine mineralization

As depicted in Fig. 3, simazine decomposition was significantly ($P < 0.05$) decreased in soil amended with fresh and aged biochar than in the unamended soil. This implies that biochar could lessen the biodegradation of pesticides due to its adsorption capabilities. This is corroborated by the previous studies, where adding biochar to the soil significantly reduced the decomposition of simazine (Cheng et al., 2017, 2022; Khalid et al., 2020). Compared with the unamended soil, simazine decomposition in fresh treatment was significantly reduced by 4.32% ($P < 0.05$). Simazine mineralization was decreased by 2.76% in the aged treatment compared to the control ($P < 0.05$). This finding suggests that biochar aging can weaken its capacity to adsorb herbicides. This is because weathering affects surface area, pore volume, functional groups, and the overall structure of the biochar. Adding biochar to the soil can significantly decrease pesticide mineralization. However, the adsorption capacity of biochar may be reduced due to weathering, thereby reducing its ability to absorb simazine in the soil.

In the adsorption experiment, it was observed that there was no clear and significant difference ($P > 0.05$) between the soil amended with aged biochar and the soil amended with fresh biochar to retain simazine in the solution (Fig. 1). However, there was a significant and remarkable difference observed between the control group and the other two treatment groups in the simazine sorption to the solid phase in agricultural soil ($P < 0.05$). Jones et al. (2011) concluded that fresh and aged biochar are equally susceptible to an abiotic herbicide breakdown due to their similar pH levels. This study found that the pH of aged biochar was significantly lower than that of fresh biochar. This study showed that more simazine decomposition happened in aged biochar treatment compared to fresh treatment due to the lower alkaline content, one of the properties that have the most significant impact on biochar (Fig. 3). According to PLFA analysis (Fig. 4), biochar aging not only influenced microbial biomass ($P < 0.05$) but also altered the structure of the microbial community in the soil. This evidenced that the aging of biochar in the field can lead to a shift in the microbial community, which regulates the process of simazine mineralization. However, further study is required to investigate this inference. This result confirms that aging could alter biochar properties, resulting in the high decomposition of simazine and regulating the microbial community.

The structural changes in the fourier transform infrared radiation (FTIR) spectra of aged and fresh biochar are illustrated in Fig. 5. Based on the processes used by Mohamed et al. (2017) and Twagirayezu et al. (2022) to analyze FTIR, fresh biochar exhibited a more noticeable and relative solid intensity than the aged biochar. This could be due to several functional groups such as O–H and/or N–H stretching, aliphatic C–H group stretching, and polysaccharides or polysaccharide C–O stretching compounds in fresh biochar. Therefore, aging processes can alter biochar structure, decreasing its capacity to adsorb herbicides.

3.4. The effects of aged biochar on soil microbial structure, community, and abundance

As represented in Table 2, gram-positive bacteria in aged and fresh treatments decreased slightly by 1.01 times for each relative to those in control. No significant difference ($P > 0.05$) was observed between aged and fresh treatments. Compared with the control, gram-negative in aged and fresh treatments were significantly higher by 1.02 and 1.04 times, respectively ($P < 0.05$). Relative to the control, fungi were significantly increased ($P < 0.05$) by 1.02 in aged treatment and significantly decreased ($P < 0.05$) 1.21 times in fresh treatment. AMF in aged and fresh biochar treatments increased dramatically by 1.03 and 1.16 times compared with the control ($P < 0.05$). Actinomycetes in aged and fresh biochar treatments decreased substantially by 1.01 and 1.03 times, respectively, compared with the control ($P < 0.05$). Relative to the control, eukaryotes in aged and fresh biochar decreased by 1.02 and 1.14 times, respectively. These findings demonstrated that adding aged

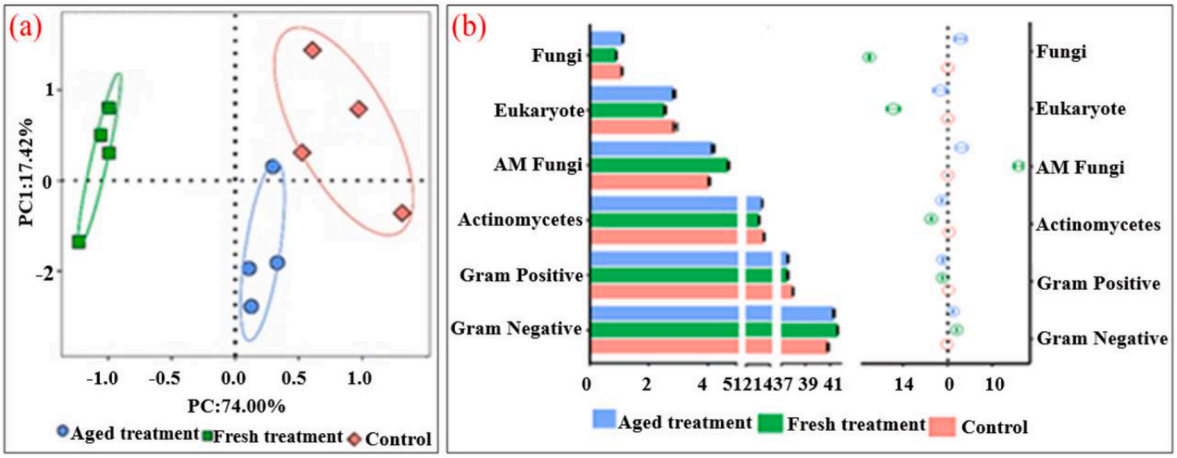

Fig. 4. The principal component analysis of PLFA for the effects of fresh and aged biochar on microbial community structure in the soil (a) and the relative abundance of each microbial group (b).

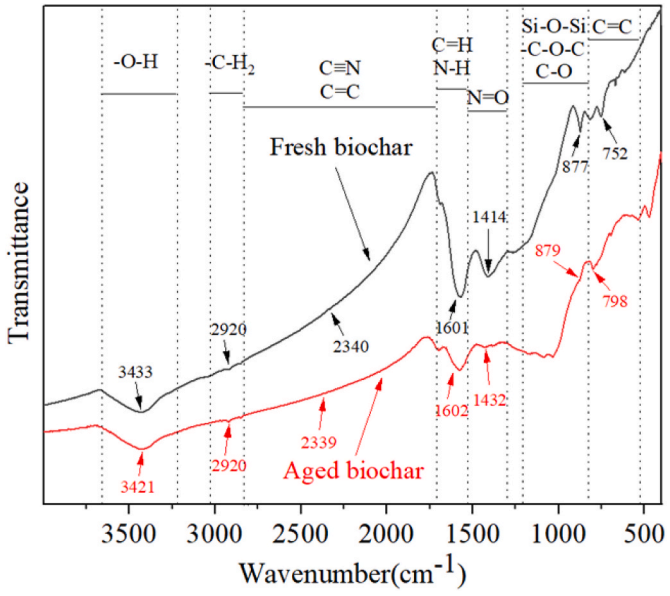

Fig. 5. Representative FTIR of spectra for fresh and aged biochar.

Table 2
Influences of fresh and aged biochar on the relative abundance of microbial groups in the soil. All values presented are mean and standard deviations (n = 4). A significant difference (*t*-test, $P < 0.05$) between the three groups is represented by superscript letters behind the data

	Control	Aged treatment	Fresh treatment
Gram+	37.95 ± 0.06^a	37.53 ± 0.08^b	37.52 ± 0.08^c
Gram-	40.83 ± 0.10^a	41.71 ± 0.10^b	42.35 ± 0.05^b
Fungi	1.09 ± 0.03^a	1.12 ± 0.02^c	0.90 ± 0.00^b
AMF	4.06 ± 0.05^a	4.18 ± 0.05^c	4.70 ± 0.05^b
Actinomycetes	13.18 ± 0.05^a	13.01 ± 0.03^c	12.69 ± 0.05^b
Eukaryotes	2.90 ± 0.11^a	2.85 ± 0.07^c	2.54 ± 0.06^b

and fresh biochar to the soil could affect microbial populations differently. The increased abundance of gram-bacteria and AMF in the fresh treatment could be attributed to the larger pore volume and surface area of the biochar.

Soil microbial community structures in control, aged, and fresh biochar groups were grouped in different quadrants (Fig. 4a). These results indicated that adding fresh and aged biochar can change the microbial community structure differently in the soil environment. This may be due to aging processes that altered the structure, biochar surface, and porosity, which could be a potential home for microorganisms, protecting them from predation. As shown by the results illustrated in Fig. 4b, aged and fresh biochar significantly changed the relative abundance of fungi and eukaryotes separately. Fresh and aged biochar increased the amount of AM F in the soil, but fresh biochar showed a more significant effect than aged biochar. Adding fresh and aged biochar to the soil resulted in a slight change in Actinomycetes and Gram-positive bacteria. Fresh biochar increased gram-negative bacteria slightly more than aged biochar compared with the control. Ultimately, adding aged biochar to the soil could alter the microbial community and structure, affecting the concentration of pesticides in the soil.

3.5. *Mechanisms of biochar aging regulating the fate of simazine in soil environments*

There is excellent scientific significance in evaluating the environmental behavior and application value of biochar in the remediation of pesticide-contaminated soil (Khalid et al., 2020). Typically, the mechanisms by which biochar regulates the pesticide concentration in the soil environment include adsorption (Mia et al., 2017b), shielding, and blocking contact between the microbial community and the pesticide (Ali et al., 2019). This could significantly influence the adsorption of pesticides onto biochar (Fig. 1) and could also change the microbial community and diversity (Fig. 4a), affecting simazine decomposition (Fig. 3). For instance, Mia et al. (2017a) have reported that the aging processes can reduce the adsorption capability of biochar. This can result in increased contact between simazine and microorganism decomposers. In addition, the amount of simazine in the leachate can also be increased (Fig. 2).

This study has shown that biochar aging can positively and negatively affect the soil environment by regulating pesticide content. It can alter the physicochemical properties of biochar, such as cation exchange capacity, specific surface area, and porosity, decreasing the content of pesticides that can be adsorbed by biochar (Wang et al., 2020). This may increase the free pesticides in the soil, resulting in a high probability of contact between pesticides and microorganisms (Ali et al., 2019). It can change the composition of trace elements and microbial community structure in the soil (Fig. 4a). This may reduce the retention of pesticides in the soil, increasing the pollution risk in other compartments, such as surface and underground watercourses. Therefore, the positive and negative effects of aging should be carefully considered when treating pesticide-contaminated soil through biochar application.

4. Conclusion

The findings obtained from this study have confirmed that field-aging can change the influence of biochar on herbicide behavior and soil microbial community structure. Aged biochar decreased the SSA from 46.04 m^2 g^{-1} to 38.16 m^2 g^{-1}, indicating a loss of structural integrity of the biochar. Aged biochar could reduce the leaching of simazine in the soil; however, its average proportion of adsorbed simazine was significantly lower at 4.8% than fresh biochar. Aging can alter the physicochemical properties of fresh biochar, reducing its ability to decrease the mineralization of simazine in the soil by 1.66%. Aging of biochar reduced Gram-positive and AMF bacteria, which play an essential role in the mineralization and decomposition of simazine. This study suggests that burying biochar for a long time can diminish its potential to interact with insecticides. This could be limited by producing fresh biochar and using it directly to effectively combat pesticides that remain in the soil after fighting against soil-borne plant pests. However, further research is needed to fully understand the specific mechanism by which aged biochar affects the composition of the microbial community in the soil.

Credit author statement

Hongguang Cheng: Methodology, Investigation, Data curation, Validation, Writing – original draft.; Dan Xing: Conceptualization, Methodology, Writing – review & editing, Project administration, Supervision, Funding acquisition.; Gratien Twagirayezu: Formal analysis, Data curation, Software.; Shan Lin: Visualization, Investigation, Formal analysis, Data curation, Writing – review & editing.; Shangyi Gu: Visualization, Data curation.; Chenglong Tu: Supervision, Software, Validation, Resources.; Paul W. Hill: Resources, Methodology, Visualization.; David R. Chadwick: Data curation, Investigation.; Davey L. Jones: Resources, Data curation, Methodology.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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