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Full length article

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PII: S0160-4120(24)00717-7
DOI: <https://doi.org/10.1016/j.envint.2024.109131>
Reference: EI 109131

To appear in: *Environment International*

Received Date: 20 June 2024
Revised Date: 15 August 2024
Accepted Date: 4 November 2024



Please cite this article as: J. Wang, T. Norgaard, L. Pugliese, P.N. Carvalho, S. Wu, Global meta-analysis and machine learning reveal the critical role of soil properties in influencing biochar-pesticide interactions, *Environment International* (2024), doi: <https://doi.org/10.1016/j.envint.2024.109131>

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Global Meta-Analysis and Machine Learning Reveal the Critical Role of Soil Properties in Influencing Biochar-Pesticide Interactions

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Abstract

Biochar application in soils is increasingly advocated globally for its dual benefits in enhancing agricultural productivity and sequestering carbon. However, lingering concerns persist regarding its environmental impact, particularly concerning its interactions with pesticide residues in soil. Previous research has fragmentarily indicated elevated pesticide residues and prolonged persistence in biochar-amended soil, suggesting a potential adverse consequence of biochar application on pesticide degradation. Yet, conclusive evidence and conditions for this phenomenon remain elusive. To address this gap, we conducted a comprehensive assessment using meta-analysis and machine learning techniques, synthesizing data from 58 studies comprising 386 observations worldwide. Contrary to initial concerns, our findings revealed no definitive increase in pesticide concentrations in soil following biochar application. Moreover, a significant reduction of 66% in pesticide concentrations within soil organisms, such as plants and earthworms, was observed. The quantitative analysis identified soil organic matter content as a key factor influencing biochar-pesticide interactions, suggesting that applying biochar to soils rich in organic matter is less likely to increase pesticide persistence. This study provides a critical assessment of the environmental fate of pesticides under biochar application, offering valuable guidance for the optimal utilization of both pesticides and biochar in sustainable agricultural practices.

Keywords: meta-analysis, machine learning, biochar, pesticide behavior, persistence, bioavailability.

1. Introduction

Biochar is a carbonaceous material produced through the pyrolysis of biomass in an oxygen-limited environment. In recent years, biochar has become a popular soil amendment for agricultural use due to its ability to improve soil properties, overall fertility and carbon sequestration (Ali et al., 2017; El-Naggar et al., 2019; Singh et al., 2010; Zhu et al., 2021). Its economical and environmentally friendly characteristics offer a promising future for increasing crop yields and reducing greenhouse gas emissions. However, the widespread application of biochar in soil could potentially lead to some unintended consequences and environmental risks. In particular, it has been observed that biochar application could change the environmental behavior of agrochemicals like pesticides (Bošković et al., 2022; Gu et al., 2016; Kookana et al., 2011).

Pesticides have become essential in agriculture, playing a crucial role in meeting the increasing food demands caused by the explosive demographic growth in the 20th century. However, the growing usage of pesticides has raised environmental concerns (FAO, 2022). The high persistence and toxicity of pesticides in soil can result in severe ecological consequences, especially their accumulation in the food chain, which poses significant risks to human health (Kalyabina et al., 2021). Furthermore, the migration of pesticides from agricultural fields to surface water and groundwater sources amplifies their environmental impact, threatening the entire ecosystem. The European Environment Agency (EEA) has reported that more than one pesticide was detected above the effect threshold at 10%-25% of all surface water monitoring sites and at 4%-11% of the groundwater monitoring sites in European countries (EEA, 2024).

Beyond enhancing soil properties and crop production, biochar application can effectively limit pesticide mobility and the probability of pesticides spreading into the environment. However, the long-term impact of biochar on the environmental fate of pesticides remains unclear (Liu et al., 2018), with some studies suggesting beneficial outcomes and others indicating potential risks. On one hand, the presence of biochar in the soil can make pesticide less bioavailable for microbes and plants (Wang et al., 2018; Cervantes-Díaz et al., 2024; Wu et al., 2019). This effect is attributed to biochar's high porosity and large specific surface area, which can strongly adsorb pesticide molecules and shield them from biodegradation (Liu et al., 2018). Consequently, applying biochar in the fields may cause increased pesticide residues in the soil and a higher risk of allowing these pesticides into the food chain (Li et al., 2018; Safaei Khorrām et al., 2016). However, a few studies observed a contradictory phenomenon with decreased pesticide concentration in biochar-amended soil (Sarker et al., 2023; Wu et al., 2019), since biochar may serve as an electron shuttle in biochemical processes in soil, accelerating the pesticide biochemical degradation (Kappler et al., 2014; Ren et al., 2023; Yuan et al., 2022). Previous literature also suggested that a possible mechanism for enhanced microbial degradation rates of sorbed pesticides could be due to biochar functionality in boosting soil microbes and enzyme activities (Lopes et al., 2021).

The diverse properties of biochar, soil, and pesticides across studies pose a significant challenge in determining the impacts of biochar on the environmental behavior of pesticide residues, making it difficult to generalize the results. Certain studies have attempted to synthesize existing research and examine pesticide degradation in biochar-amended soils (Nighojkar et al., 2023; Song et al., 2023). However, they often overlooked the substantial

influence of heterogeneous soil properties and inherent physicochemical properties of pesticides. Consequently, the current understanding and evidence regarding the interactions between biochar and pesticide residues may be inherently biased, as solely focusing on biochar properties is inadequate.

The objective of this study is to systematically assess the interactions of biochar application in soil on the environmental behavior of pesticide residues, such as persistence and bioavailability to soil organisms. The concentration of pesticide residues in soil and concentration in organisms (e.g. plants and earthworms) were chosen as indicators of persistence and bioavailability to assess the impact of various biochar applications in agriculture. Various influencing factors, such as soil environmental conditions, inherent properties of the pesticides, and characteristics of the biochar, have been gathered for quantitative analysis. By investigating the interplay between biochar and pesticides across different soil conditions, this study serves as a reference for implementing a more informed and responsible strategy for biochar application.

2. Methods

2.1 Literature search and data collection

The databases used for data collection were Web of Science and Scopus, which are considered among the most comprehensive libraries for academic searches. The search incorporated combinations of the keywords such as “biochar,” “pesticide”, “biodegradation,” “bioaccessibility,” “bioavailability,” and “uptake,” including only publications in English from January 2014 to December 2023. The search query can be found in supporting information (Text S1). With this searching strategy, 185 publications in Web of Science and 272 publications in Scopus were found. Ultimately, 320 publications were included after deleting the duplicates.

The screening of the literature consisted of the following steps (Figure S1): publications were first screened by reading the title and abstract, resulting in the exclusion of 182 publications due to their low relevance. Afterward, the literature was screened again by reviewing the full-text content. The inclusion criteria were as follows: 1) The study includes testing pesticide residues in both the control group without biochar and the treatment group with biochar. 2) The experiments must be done with at least 2 replicates. 3) The experiments must be done in a matrix (soil) which involves both adsorption and biodegradation processes. In total 58 studies were finally included in the study and 386 pairwise observations with control and treatment data of concentration of pesticide soil residues (containing 245 pairwise datasets) as well as concentration in organisms (containing 141 pairwise datasets) were extracted from the articles. The data from the graphs were digitized and extracted with WebPlotDigitizer (Rohatgi, 2022). The parameters related to soil, biochar, and pesticide physiochemical properties were also extracted. The list of studies included were listed in Table S4 and the software VOS viewer version 1.6.20 (van Eck and Waltman, 2010) was employed for clustering keywords and academic terms within the titles and abstracts of these publications.

2.2 Data treatment

To facilitate data comparison, soil organic matter (SOM) was calculated using soil organic carbon divided by van Bemmelen factor of 0.58 (Heaton et al., 2016). The biochar application rate was converted from “t/ha” and “kg/ha” to percentage using Equation 1.

$$\text{Application rate (\%)} = \text{AR}/(\text{h}\times\rho) \quad (\text{Equation 1})$$

where AR is the application rate with the unit of kg/ha., h is the application depth (10 cm) and ρ is the soil bulk density of 1.5 g/cm³ (Schjønning et al., 2023).

The collected data were grouped according to biochar properties and soil conditions. Pyrolysis temperatures were categorized as low (<300 °C), medium (300-500 °C) and high (>500 °C). Application rates were grouped as <0.5 %, 0.5-2 %, 2-5 % and >5 %. Soil pH was categorized as low (pH<6), medium (pH=6-8) and high (pH>8). SOM levels were classified as low (<2 %), medium (2-4 %) and high (>4 %). We also categorized the raw materials used for biochar production. Manure and sludge, as well as food waste, were classified as biowaste materials. Various types of wood and nutshells were categorized as lignocellulosic biomass. Meanwhile, herbaceous plants and straws were classified as herbaceous biomass. The organisms were grouped as plants, earthworms, and vertebrates. Several studies that used resins to simulate

the biotic uptake of pesticides and predict pesticide accumulated concentration in soil organisms (Maletić et al., 2022; Ranguin et al., 2020) were also considered in the analysis. Additionally, we categorized the pesticides based on their characteristic functional groups, exploring how the behavior of triazole, triazine, organochlorine, organophosphorus, and organofluorine pesticides change in biochar-amended soil. The variable groupings for these categories are shown in the Table 1.

2.3 Meta-analysis

The package Metafor in R v.4.3.2 was used for the data treatment (Viechtbauer, 2023). To evaluate the effect of biochar application across a wide range of parameters, the natural logarithm ratio of the response variable (concentration of pesticide residues in soil and concentration in organisms) between control and treatment (lnRR) was used to normalize and compute the effect size (Equation 2) (Hedges et al., 1999). A positive effect size indicates an increase in the mean of variables with biochar application compared to the case without biochar application.

$$\ln RR = \ln(X_t/X_c) \quad (\text{Equation 2})$$

Where X_c and X_t are the means of the response variables (soil residue concentration or concentration of pesticides in organisms) in the control and treatment, respectively. The random effect model was used in the analysis.

The inversed variance ($1/v$) is used to weigh each study's effect. Studies with lower variance (i.e., more precise estimates) are given more weight, as they are considered to provide more consistent and reliable evidence. The variance of lnRR is estimated by Equation 3.

$$v = \frac{S_t^2}{n_t X_t^2} + \frac{S_c^2}{n_c X_c^2} \quad (\text{Equation 3})$$

Where v is the variance of the effect size, S_t and S_c is the sample variance of the treatment group and control group, n_t and n_c are the sample size of the treatment group and control group. The pooled effect sizes for the individual groups and the whole dataset were evaluated with a random effect model and visualized by the forest plots. Groups with fewer than 3 observations were excluded from the forest plots. Considering the variance between the literatures, a multivariate Meta-Analysis model was used to calculate the effect size. The restricted maximum likelihood (REML) method was used to estimate the heterogeneity variance. The pooled effect sizes were plotted with error bars of 95% confidence interval in the forest plot. The missing values of standard deviation (SD) were inserted by the method according to Bracken (1992) with the Metagear package (Lajeunesse, 2021). In our study, a two-level meta-analysis was conducted with the rma.mv function in the Metafor package for calculating the overall effect size. It was assumed that individual effect sizes were nested within groups of the studies which has the same author. The mean of lnRR was transformed back to the percentage of change by biochar application with Equation 4 for easier interpretation. The 95% confidence interval in percentage was calculated from the standard error (SE) transformed by applying a first-order Taylor expansion (Equation 5).

$$\text{percentage change} = [\exp(\ln RR) - 1] \times 100 \quad (\text{Equation 4})$$

$$SE(RR) \approx \exp(\ln RR) SE(\ln RR) \quad (\text{Equation 5})$$

The forest plot for grouped variables can provide a clear visual representation of the effect for grouped variables. However, it is not enough to examine complex interactions between multiple variables. To explore the relationship between effect size with different biochar, soil and pesticide properties, the data was fitted to the mixed-effects models, which consider both variability caused by the fixed effect between covariates and the random effect between different studies. Different parameters related to the biochar, pesticides and soil properties were chosen as moderators. According to an essential procedure of meta-analysis introduced in Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) (Page et al., 2021), the publication bias must be evaluated to ensure the reliability of the analysis. Egger's test provides a statistical method for detecting bias in meta-analysis and a significant ($p < 0.05$) linear relationship can indicate the presence of publication bias in a meta-analysis. Publication bias for the overall effect size of pesticide residue concentrations and accumulated pesticide concentration in soil organisms was assessed by Egger's regression test by doing the linear regression from effect size on its standard error weighted by the inversed variance (Egger et al., 1997).

2.4 Quantitatively analysis of variables' importance

Due to the limitations of meta-linear regression, which only considers the impact of individual variables on the outcome, we used the "metaforest" package (Lissa, 2020) in R which is adapted from a machine learning algorithm by incorporating the weight of each observation to bootstrap sampling for multiple variables. This package can be used to explore the importance of moderators causing heterogeneity from several potential candidates in meta-analysis. Before implementing the metaforest model, to ensure an adequate dataset for robust training, only those variables with less than 40% missing values were included because the Metaforest package requires a complete dataset for training. Additionally, pairwise Pearson correlation tests were conducted across all parameters, and from each pair with a correlation coefficient greater than 0.75, only one parameter was retained. The importance of these parameters was calculated through the bootstrap algorithm in the Metaforest package, iteratively refining the set of variables by conducting 100 rounds of model fitting and variable elimination to identify robust parameters.

2.5 Prediction of the effect of biochar application by random forest models

Factors ranking in the top 40% were selected for inclusion in the training of the random forest model to ensure a focus on the most influential factors and to incorporate more datasets with complete data for training. This training was conducted with the "ModelInfo_mf" function in the machine learning package "Caret" (Kuhn et al., 2023) in R. The 'ModelInfo_mf' function tunes the model by considering all three types of effects: uniform, fixed effects, and random effects. A tuning grid was used to select the optimal hyperparameters in the random forest model by varying two parameters: the number of variables considered at each split ('mtry'), and the minimum size of the terminal nodes ('min.node.size'). Ten-fold cross-validation was implemented to estimate model reliability and stability. The model with the lowest root mean square error (RMSE) value was selected as the final model. The model's predictive accuracy was reported using the RMSE and coefficient of determination (r^2). To ensure the robustness and optimal performance of our model, the convergence plot was used to monitor and assess

the algorithm's progress and stability across iterations. Furthermore, the relative importance of each variable in the final model was estimated again, and partial dependence analysis was conducted to interpret and illustrate how the factors influenced the effect sizes.

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3. Results

3.1 The overall effect of biochar application on pesticide behavior in soil

In total 58 studies were included in this study, generating 245 effect sizes for soil pesticide residue concentration and 141 effect sizes for accumulated concentration in soil organisms (Figures 1b and c). The geographic distribution of these studies shows that the majority of investigations took place in Asia, Europe, and America (Figure 1a). Moreover, this compiled dataset incorporated various experimental setups such as incubation, pots, columns and fields, and comprehensively examined the effects of biochar application in different soil environments and on various soil organisms. The extensive range and methodological diversity enhanced the global relevance of our meta-analysis, ensuring that the findings are applicable across different agricultural regions and environmental conditions.

Assessing publication bias is essential in meta-analysis to ensure the reliability of findings, as studies with favorable outcomes are more likely to be published, potentially skewing conclusions (Thornton and Lee, 2000). To address this critical issue, we first employed Egger's regression test, a widely recognized statistical method that evaluates this bias by regressing standardized effect estimates against their precision. The results of Egger's test (Table 2) showed no significant publication bias in our dataset for meta-analysis ($p > 0.05$) and the overall effect sizes derived from our meta-analysis are likely not influenced by selected publications, contributing to the reliability of our results in the following sections.

As shown in Figure 1b, the meta-analysis yielded an overall effect size of 6.01%, with a 95% confidence interval of -25.84% to 37.87%, which does not allow us to draw definitive conclusions about the impact of biochar on pesticide residues in soil. The symmetrical distribution of points from negative to positive indicates no apparent bias; however, the wide confidence interval reflects substantial variability across studies, potentially due to factors such as study design, biochar properties, and soil conditions. Moreover, this lack of statistical significance consistently persisted across all grouped experimental setups (Figure 1d), which included both positive and negative mean effect sizes. These findings challenge the common concern that biochar application leads to increased pesticide persistence in the soil. Instead, our results suggest that biochar application in soil may not always increase the concentration of pesticide residues in the soil.

However, biochar application significantly reduced the concentration of pesticides across all types of organisms, including plants, earthworms, and vertebrates, by 70%, 48%, and 55%, respectively. Experiments utilizing resin to simulate pesticide uptake by soil organisms also demonstrated a significant 30% reduction in concentration. The overall effect size averaging all considered soil organisms shows that biochar application in soil can significantly reduce pesticide concentration in soil organisms by 66% (Figure 1c). This reduction was observed across different experimental setups: a 72% decrease was seen in incubation experiments and a 43% reduction in pot experiments. However, in column experiments, the reduction did not reach statistical significance, likely due to the large deviations in the limited dataset ($n=4$). Based on these results, we could infer that applying biochar to soil can effectively reduce the impact of pesticides on soil health, which is beneficial for both the ecosystem and human health by reducing bioaccumulation through the food chain.

3.2 Influencing factors

3.2.1 Response of pesticide behaviors to biochar application differs by pesticide types

The toxicity and behavior of pesticides are influenced by their functional groups, which decide their mode of action, environmental persistence, and effects on non-target organisms, including humans. Through a review of relevant publications, we have classified commonly studied pesticides into five main types based on their characteristic functional groups: triazole, triazine, organophosphorus, organofluorine, and organochlorine pesticides (Figure 2a). Our findings demonstrate that the influence of biochar application on pesticide residues in soil varies depending on the type of pesticide involved. We observed increased concentrations of pesticide residues in the triazole, organochlorine, and organofluorine groups, whereas reduced concentrations were noted in the triazines and organophosphorus groups. Notably, among these pesticide types, a significant decrease in soil concentration was observed within the triazine group, with pesticide residue decreasing by 37% following biochar application.

In terms of pesticide accumulation in organisms, biochar application led to significant reductions in the concentrations of triazole, organophosphorus, organofluorine and organochlorine by 54%, 84%, 43% and 48%, respectively (Figure 2g). However, the reduction was not statistically significant for triazine. The unique behavior of triazines in biochar-amended soil might be attributed to their relatively hydrophilic nature compared to other types of pesticides that are more lipophilic.

3.2.2 Response of pesticide behaviors to application rates and types of biochar

Variability exists in how different application rates affect pesticide behavior (Rasool et al., 2022), yet no significant effect was detected across all grouped application rates, spanning from less than 0.5% to more than 5% (Figure 2b). This suggests that higher rates of biochar application don't necessarily lead to increased pesticide persistence. Instead, biochar might aid in the microbial degradation of pesticides, potentially offsetting the increased retention of pesticides by biochar application.

A more detailed analysis was conducted to investigate the diverse effects influenced by biochar properties. This involved categorizing biochars based on their feedstock materials and pyrolysis temperature. It was discovered that biochars made from lignocellulosic material significantly increased pesticide residues in soil by 20% (Figure 2c). Conversely, biochars derived from herbaceous and biowaste materials didn't have a significant impact on pesticide residues. Similarly, no significant changes in pesticide residues in soil were observed across all grouped pyrolysis temperatures (Figure 2d).

Pesticide accumulation in organisms showed a general decrease across all groups categorized by biochar types and application rates. For instance, the concentration of pesticides accumulated in soil organisms exhibited a significant reduction across all grouped application rates, even with minimal rates below 0.5% (Figure 2h). Biochars derived from lignocellulosic materials led to a greater reduction in pesticide concentrations in organisms, achieving decreases of 57%, compared to reductions of 41% observed with herbaceous-derived biochars (Figure 2i). Furthermore, for different pyrolyzed temperatures for biochar production, the reduction became significant when the temperature exceeded 300°C and

became more pronounced at higher pyrolysis temperatures: a 56% decrease was recorded at temperatures ranging from 300°C to 500°C, which further increased to 69% at temperatures above 500°C (Figure 2j).

3.2.3 Interactions Response to different soil characteristics

The effects of biochar application under varying soil conditions were examined by grouping soil parameters such as SOM and pH (Figures 2e and 2f). It was observed that in soils with a pH greater than 8, biochar application significantly increased soil pesticide residues by 98.6%. Conversely, under neutral (pH 6-8) and acidic conditions (pH < 6), the effect was not significant, although the effect size tended to increase with rising pH. This suggests that applying biochar in alkaline soil conditions potentially increases pesticide persistence. Additionally, a significant increase in soil pesticide residue concentration was noted in soils with low soil organic carbon (<2%), where residues increased by 66%. However, in soils with medium to high SOM (>2%), no significant impact was observed. So far, significant increases in soil pesticide residues have only been observed when biochar is applied in soils with high pH and low SOM. This underscores the critical role of soil conditions in modulating the effects of biochar application. For pesticide accumulation in organisms, the application of biochar significantly reduced pesticide levels across all pH and SOM groups (Figures 2k and 2l). However, some variations in the effect were still observed among these groups.

3.3 Relationships of responses with different factors

The forest plot provided a clear visual representation of the effects across different biochar applications. However, its ability to analyze complex interactions among multiple variables is limited. To thoroughly explore the relationship between effect size and various characteristics, such as different types of biochar, soil properties, and pesticide properties, mixed-effect models were used to regress the variables with effect sizes. Single moderators were sequentially included in the models to identify the influence of different factors on pesticide behavior in biochar-amended soil. The regression results are detailed in Table S1, and moderators with significant ($p < 0.05$) relationships are displayed in Figure 3. The subfigures in Figure 3 are displayed in a sequence from lowest to highest according to their akaike information criterion (AIC) values, which reflect the goodness of fit. Generally, we observed that a higher oxygen-to-carbon (O/C) ratio in biochar correlated with increased pesticide residue concentrations resulting from biochar application (Figure 3a). An increase in clay content and pH were found to contribute to an increase in pesticide residues (Figures 3b and 3d), whereas an increase in SOM was associated with less pesticide residues in biochar-amended soil (Figure 3c). Additionally, there was a noticeable trend indicating that pesticides with higher molecular weights tend to accumulate more in biochar-amended soil (Figure 3e). Lastly, among the variables that reached significance in the meta-regression, the application rate is the least well-fitted variable (Figure 3f). The plot displays a positive trend, indicating that higher application rates of biochar potentially lead to a greater retention of pesticides in the soil.

The meta-regression models of the effect size of pesticide accumulated concentration in organisms against various parameters are displayed in Table S2. Significant linear relationships were found between effect sizes with 3 parameters including soil clay content,

biochar surface area, and biochar application rates, which are displayed in the order of ascending AIC in Figure 4.

3.4 Key parameters influencing pesticide behavior in biochar-amended soil

To achieve a more comprehensive understanding of the multiple interactions, we employed a random forest model to analyze the importance of parameters and their interactions. Before training the model, we computed Pearson correlation coefficients (Figure 5a) for the continuous variables to screen out autocorrelated variables. The Metaforest model was then trained with the remaining 10 parameters ($n = 91$), and the importance ranking of these parameters, as determined by the model, is depicted in Figure 5b.

Given the overview of parameter importance provided by Metaforest, we further examined how the key parameters influence the effect size and utilized these parameters to predict pesticide behavior in biochar-amended soil. The top 40% of parameters—SOM, SA, pH, and FD—were selected to train the model, incorporating a total of 132 complete observations. The final model was trained and selected from the tuned models with a minimum RMSE value of 0.46. The validation plot showing the performance of the final model is presented in Figure 6b, and the convergence plot is depicted in Figure 6c. The model prediction accuracy was evaluated from the determination coefficient, R^2 , between the predicted and actual effect size, which achieved 0.69 for the final model. The model successfully converged during the training process with 7000 trees.

4. Discussion

4.1 Biochar application in soil alters pesticide persistence and bioavailability

While biochar is often seen as an effective adsorbent that reduces pesticide mobility and environmental dispersion (Dong et al., 2024; Haider et al., 2022), concerns exist about its potential to increase pesticide persistence in soil (Li et al., 2018; Safaei Khorram et al., 2016). This study represents the first attempt to compile data on pesticide residue concentrations in biochar-amended soils globally over the past decade, highlighting the varied impacts on pesticide concentrations and accumulation in soil organisms.

Overall, there was a slight tendency for biochar application to increase pesticide residues in soil when averaging all data from various conditions. The potential increase in pesticide residues is attributed to the strong adsorption between biochar and pesticides, which can decrease the bioavailability of pesticides for microbes, leading to higher concentrations of pesticide residues in soil and their longer persistence (Liu et al., 2018; Mandal et al., 2017). However, considerable variability among the selected studies arises from the diverse conditions under which these studies were conducted, including differences in biochar properties, application rates, pesticide types, soil characteristics and so on. For example, the factors regarding biochar properties such as surface area, feedstock material and O/C ratios (Figure 3a, 5b and 6a) can impact pesticide retention in soil because they largely determine its role in adsorption processes (Khalid et al., 2020; Ogura et al., 2021). Biochar derived from lignocellulosic biomass typically exhibits richer microporosity compared to other types (Leng et al., 2021). Additionally, the O/C ratio, which indicates the abundance of oxygen-containing functional groups on the biochar, also critically influences the chemisorption capabilities (Dai et al., 2021; Hassan et al., 2020). This kind of chemisorption process has considerable potential to protect pesticides from degradation and extend their persistence in the soil.

The behavior of pesticides is influenced by their lipophilicity such as K_{ow} , molecular weight, and solubility. Lipophilic pesticides generally exhibit a greater affinity for biochar, which can lead to increased retention in the biochar-amended soil (Knauer et al., 2017). Moreover, pesticides with higher molecular weights are generally less water-soluble, resulting in a greater tendency to remain adsorbed onto biochar, rather than dispersing freely in pore water (Malheiro et al., 2020). This was also proved in this study by the positive relationship between the MW of pesticides and increased pesticide residue concentrations in the soil (Figure 3e).

Biochar application in soil has significantly reduced pesticide accumulation in various soil organisms by 66% when considering all the datasets in our study. This reduction in pesticide accumulation has been consistently observed in different groups, but the extent of the reduction differed between the cases. For instance, biochar with a larger surface area appeared to be more capable of diminishing pesticide accumulation in soil organisms (Figure 4b). Moreover, the biochar produced at temperatures below 300°C did not significantly reduce the accumulated concentrations in organisms, but the reduction became significant when the pyrolysis temperature exceeded 300°C (Figure 2j). The reduction becomes more pronounced at higher temperatures, largely because biochar produced at higher temperatures typically has a larger surface area (Leng et al., 2021).

Applying more biochar did not lead to a greater decrease in the concentration of pesticides accumulated in organisms. In fact, with increasing application rates, the concentration of pesticides in organisms approaches levels found in soils without biochar application (Figure 4c). The effect of biochar application on reducing uptake by organisms became insignificant when the application rate reached over 5%. However, in agricultural practice, most applications involve rates much lower than 5%, which means that in real-world conditions, a significant reduction effect could be expected. The reasons why the effectiveness diminishes with higher application rates are not well understood yet, and this is an area where further investigation into the mechanisms is needed.

4.2 Soil properties significantly change the interactions between pesticides and biochar

Our study underscores the vital role of soil conditions in influencing pesticide behavior in biochar-amended soils. Soil organic matter, pH and clay content were identified as important factors that govern the impact of biochar application on pesticide residue concentrations in soil (Figures 3c and 5b).

Generally, applying biochar to soils, characterized by higher levels of SOM and neutral pH, tends to mitigate the potential adverse impacts of prolonged pesticide persistence. In soils with higher levels of SOM, biochar application is less likely to enhance pesticide persistence (Figures 3c and 6a). Additionally, biochar can alter the distribution of microbes in the soil by forming aggregates. Previous studies have demonstrated that biochar can concentrate and retain soil nutrients within itself, thereby creating aggregates that act as microbial hotspots. (Hagemann et al., 2017; Weng et al., 2022). The soil with higher nutrient levels can further promote these hotspots formation and boost microbial colonization on biochar surfaces (illustrated in Figure 7). The environment within these hotspots has been proven to effectively enhance the biodegradation of pesticides (Grundmann et al., 2007).

Moreover, soil pH is linked to pesticide accumulation in biochar-amended soil (Figure 3d), with soils of medium pH range between 6 to 7.5 showing a lower potential for increased pesticide residues following biochar application (Figure 6a). Higher concentrations of pesticide residues can be found when biochar is applied in alkaline soils. This is probably because low SOM content is commonly found in alkaline soils (Lu et al., 2021) which generally exhibit a lower microbial activity. The increased pesticide residue concentration can also potentially happen at very low soil pHs below 5 after biochar application. This may be because, in acidic conditions, pesticides are more likely to acquire a positive charge, which then further enhances their affinity for the negatively charged surface of the biochar (Xiao et al., 2018). The stronger adsorption interaction further shields the pesticides and makes them less bioaccessible.

Additionally, clay content also influences pesticide behavior in biochar-amended soils and it is positively related to the increased soil pesticide residues and accumulation in the organisms (Figures 3b and 4a). Applying biochar to soils with high clay content actually tends to retain more pesticides compared to its application in soils with lower clay content. This phenomenon may be due to the enhanced adsorption capabilities from the interactions between clay and biochar particles, making clay-biochar composites more efficient at adsorption than their individual pristine components (Atugoda et al., 2021; Rallet et al., 2022; Yao et al., 2014). The enhanced adsorption enabled biochar protects the pesticides better

from microbial degradation. Additionally, applying biochar to soils with higher clay content may mitigate the reduction of pesticide bioaccumulation in organisms (Figure 4a), due to increased retention of pesticides in the soil, thereby increasing the exposure of organisms to these chemicals.

5. Conclusions and Perspectives

This study compiled 386 observations from research conducted around the world, incorporating meta-analysis and machine-learning techniques to explore the complex interactions between biochar application and pesticide behavior in soils. Focusing on the influences of soil, biochar, and pesticide properties, the findings offer a valuable reference for assessing the environmental impacts of biochar application on pesticide behaviors. The main conclusions drawn from our analysis include:

- There is no definitive increase in pesticide concentrations in soil following biochar application. The retention of pesticides in biochar-amended soil largely depends on specific experimental conditions and the properties of the biochar, soil, and pesticides involved. However, biochar significantly reduces pesticide uptake by soil organisms, with clear reductions observed under various conditions.
- The persistence of pesticides in biochar-amended soil is significantly influenced by soil properties, particularly soil organic matter, pH, and clay content. Our findings suggest that higher levels of soil organic matter can reduce the risk of increased pesticide residue concentrations resulting from biochar application.
- The random forest model we have developed shows a good predictive performance with a determination coefficient (R^2) of 0.69. This model can predict the impact of biochar application on pesticide residue concentrations in soil using just four parameters: soil organic matter, feedstock material of biochar, soil pH, and the surface area of biochar.

The application of biochar in soil significantly alters the physical, chemical, and biological interactions, thereby impacting the environmental fate of pesticides. However, comprehending these interactions is complex as numerous influencing parameters modulate the outcome at the same time. While certain patterns have been discovered through our analysis, the considerable heterogeneity among experiments leaves uncertainties in conclusions. This research underscores the need for further investigation into observed patterns and underlying mechanisms to fully understand these complicated dynamics. Several key limitations need further exploration:

- 1) The impact of biochar application on the efficacy of agrochemicals remains unclear. Although biochar can reduce concentrations in soil pore water (Malheiro et al., 2020), there exists a counterbalancing effect that could decrease the levels of active substances below the threshold required for effective agricultural management (Yavari et al., 2015). This dilemma poses a significant challenge to modern agriculture, as it may necessitate an increase in pesticide usage to compensate for diminished efficacy, potentially leading to excessive agrochemical inputs into the environment. Such a scenario could ultimately disturb and harm the ecosystem by introducing more agrochemicals into the environment. Additionally, the accumulation of pesticides in the environment can

contribute to the development of pesticide-resistant pests, further exacerbating agricultural challenges.

- 2) Most studies are lab-based incubation and pot experiments, indicating a significant gap in overlooking the complexities of natural environments. Unlike the experiments isolated within a confined environment, field conditions exhibit dynamic hydraulic conditions that significantly influence the fate of pesticides. Additionally, other processes like migration, evaporation, and photodegradation in open fields can accelerate the dissipation of pesticides (Khalid et al., 2020; Müller et al., 2007). Thus, conclusions drawn from laboratory settings may not fully capture the complexity of interactions between biochar, pesticides, and the environment and potentially result in more pessimistic results than in real-world scenarios by overlooking the other dissipation processes. Therefore, a shift towards field-based research methodologies is essential to bridge this gap and provide a more accurate assessment of the practical implications of biochar application in agricultural ecosystems.
- 3) Most studies have concentrated on the short-term effects (ranging from days to months) of biochar application on pesticide behavior (Bošković et al., 2022; He et al., 2016; Manna and Singh, 2019). However, the long-term stability of biochar in soil, as well as its enduring impact on soil physicochemical processes, remain poorly understood. For example, more research is also needed to explore how biochar aging affects pesticide fates in different ways (Wu et al., 2019). Additionally, the performance of saturated biochar, and its ability to release pesticides through desorption processes (Kookana, 2010) was not thoroughly explored. Understanding the long-term implications of biochar application will enable us to make more informed decisions about its environmental impact for widespread agricultural use.

Acknowledgment

This study was performed under the project “Novel rhizosphere-activated hydroxyl radical oxidation of pesticides (OHiROOT)” supported by the Independent Research Fund Denmark [grant no. 2035-00039B].

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Figure and table captions

Figure 1. Overview of the datasets compiled from the literature.

Figure 2. Responses of the concentration of pesticide residues in soil and accumulated concentration in organisms to various groups categorized by pesticide and biochar types, and soil properties.

Figure 3. Meta-regression analysis of various parameters against the effect size of concentration of pesticide residues in soil.

Figure 4. Meta-regression analysis of various parameters against the effect size of accumulated concentration of pesticide in organisms.

Figure 5. Pearson correlation matrix of continuous parameters and parameters importance plots.

Figure 6. Partial dependence plots and validation plots.

Figure 7. Biochar's dual role in pesticide (P) interactions in soil.

Table 1. Variable groupings for pyrolysis temperature, application rate, soil pH, and soil organic matter (SOM) levels used in meta-analysis.

Table 2. The overall effect size of biochar application on pesticide residues in soil and organisms.

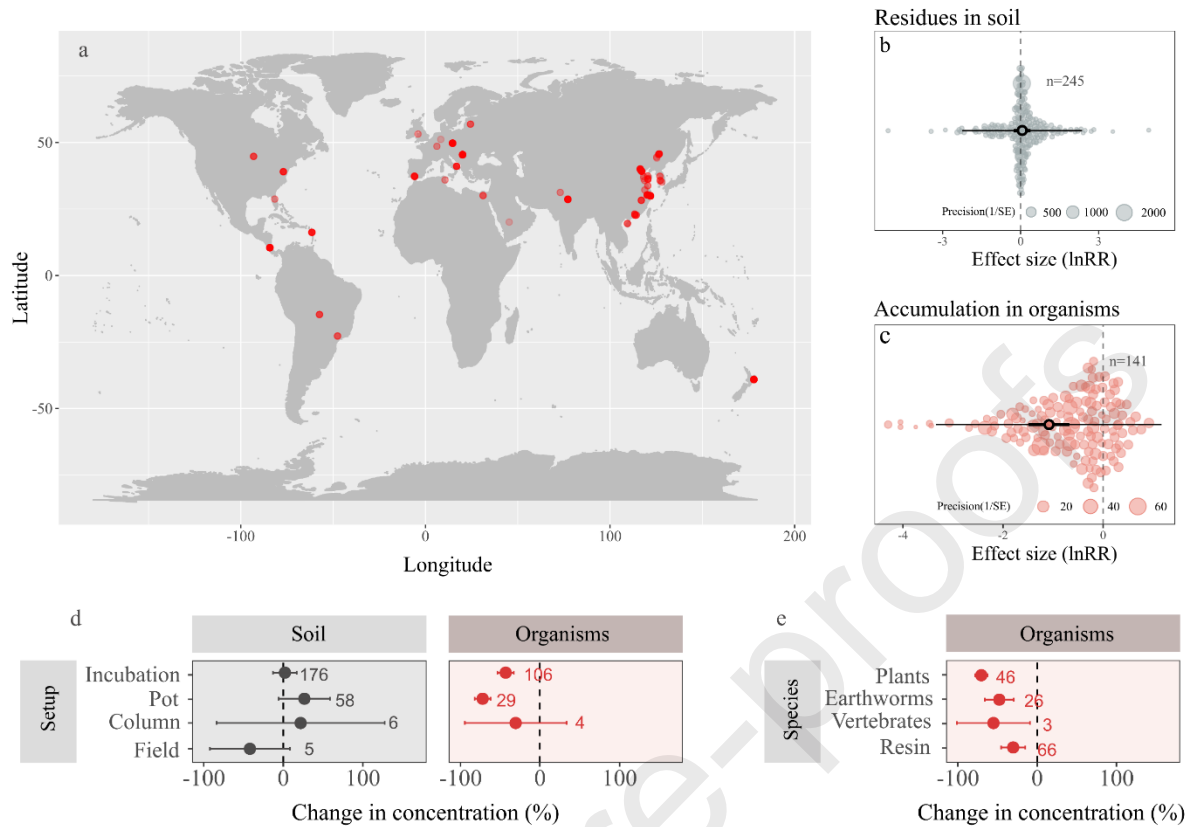


Figure 1. Overview of the datasets compiled from the literature. **a** The global distribution of the 58 studies included in the analysis. Effect sizes distribution of biochar application on pesticide behavior includes **b** soil residues concentration of pesticides (n=245) and **c** accumulated pesticide concentration in organisms (n=141). Black-circled points indicate mean effect sizes from the random effect model, with thick whiskers showing 95% confidence intervals (CI) and thin whiskers marking additional 95% prediction intervals. Light-colored circles represent individual effect sizes, scaled according to precision (inverse of the standard error). A dashed vertical line denotes the line of no effect. The forest plots display the concentration change in soil pesticide residue concentration by biochar application across **d** different experimental settings and **e** different soil lives. The numbers beside each effect size point represent the number of observations included. The error bars shown in the forest plots present 95% CI.

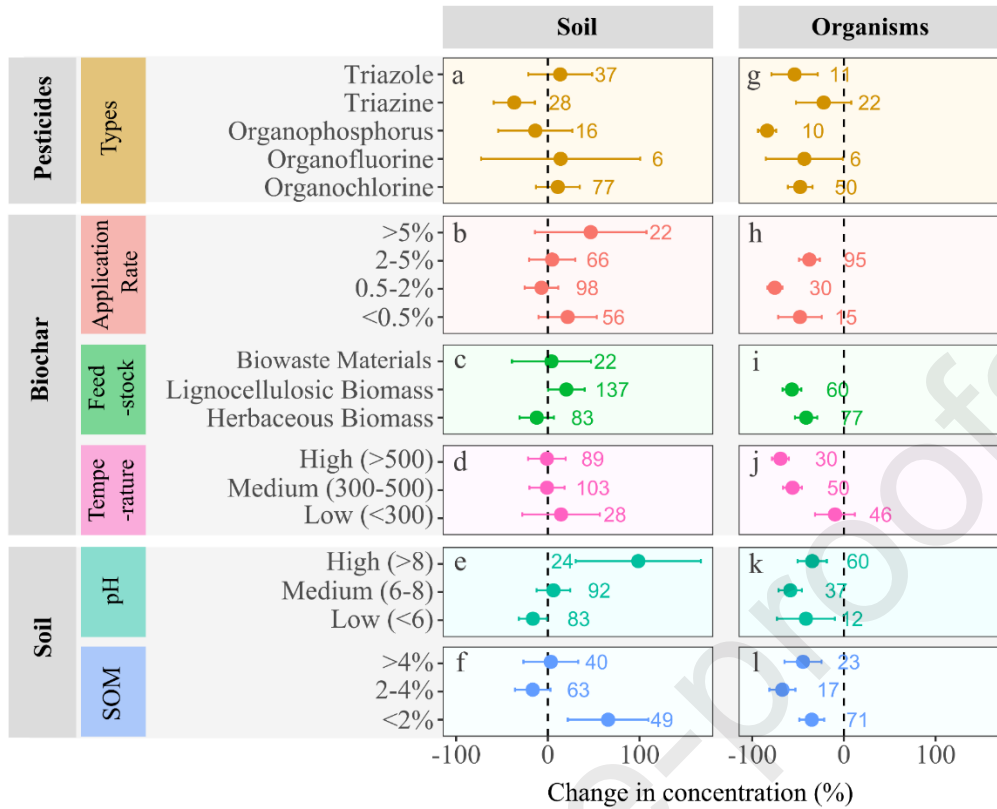


Figure 2. Responses of the concentration of pesticide residues in soil and accumulated concentration in organisms to various groups categorized by pesticide and biochar types, and soil properties. The points represent pooled effect sizes of biochar's impact on pesticide residue concentration in soil and accumulated concentration in soil organisms. The error bars show 95% confidence intervals. The numbers beside each effect size point represent the number of observations included.

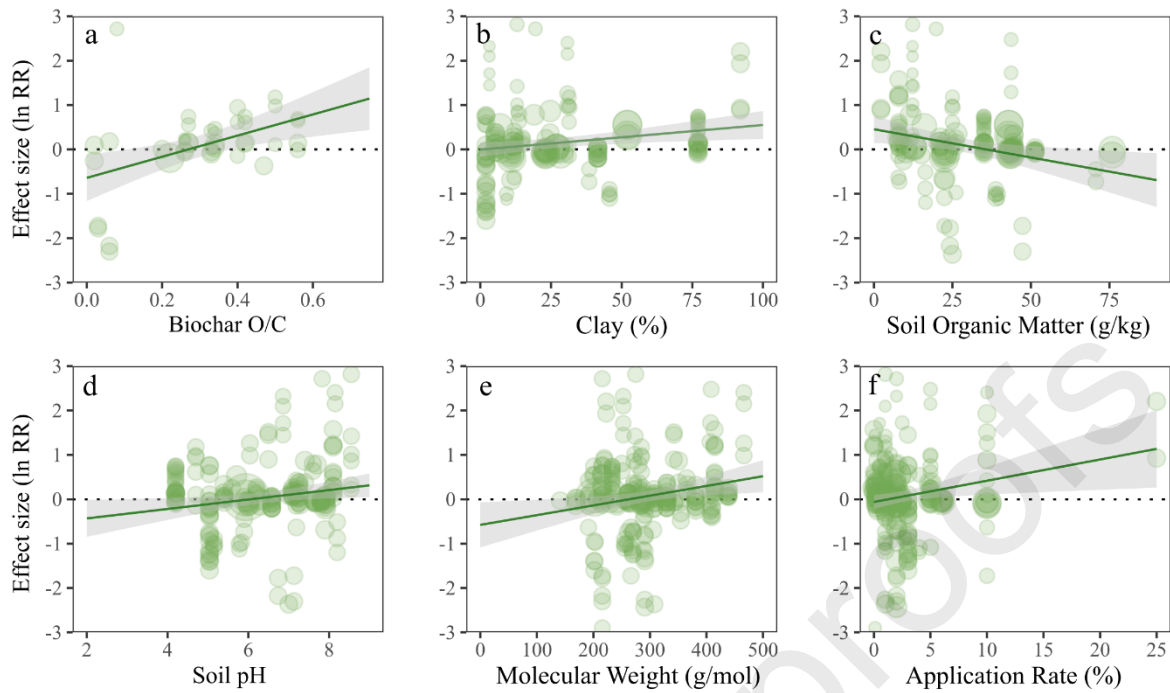


Figure 3. Meta-regression analysis of various parameters against the effect size of concentration of pesticide residues in soil. All the regressions above are significant at $p < 0.05$. The models are presented in ascending order of their Akaike Information Criterion (AIC) values. The bubble sizes in the figures correspond to the weights of the effect sizes.

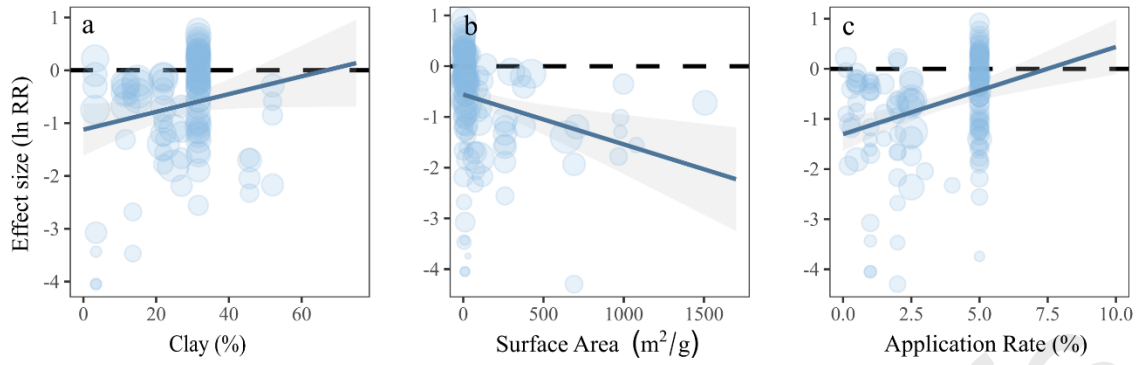


Figure 4. Meta-regression analysis of various parameters against the effect size of accumulated concentration of pesticide in organisms. The plots show parameters that achieved statistical significance at $p < 0.05$. The models are presented in ascending order of their AIC values. The bubble sizes in the figures correspond to the weights of the effect sizes.

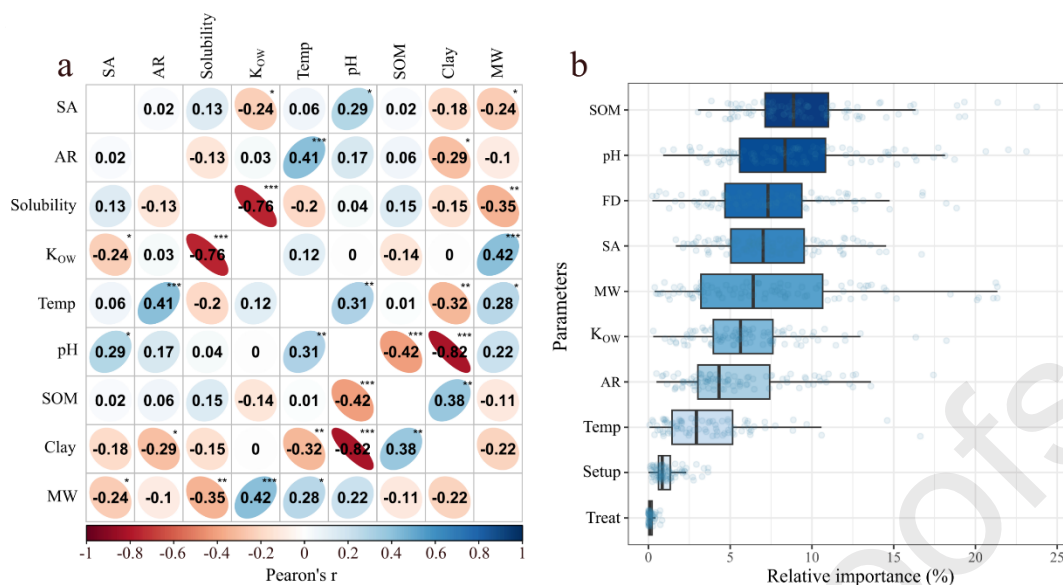


Figure 5. Pearson correlation matrix of continuous parameters and parameters importance plots. a Pearson correlation matrix of various parameters. The number of asterisks indicates the level of statistical significance: * for $p < 0.05$, ** for $p < 0.01$, and *** for $p < 0.001$. **b** The importance of different parameters evaluated by Metaforest analysis. The initial parameters include surface area of biochar (SA), application rate of biochar (AR), solubility of pesticides, logarithm of pesticide octanol-water partitioning coefficient (K_{ow}), biochar pyrolysis temperature (Temp), biochar production pretreatment (Treat), soil pH (pH), biochar production feedstock material (FD), soil organic matter (SOM), experiment setup (setup), soil clay content (Clay), and pesticides molecular weight (MW).

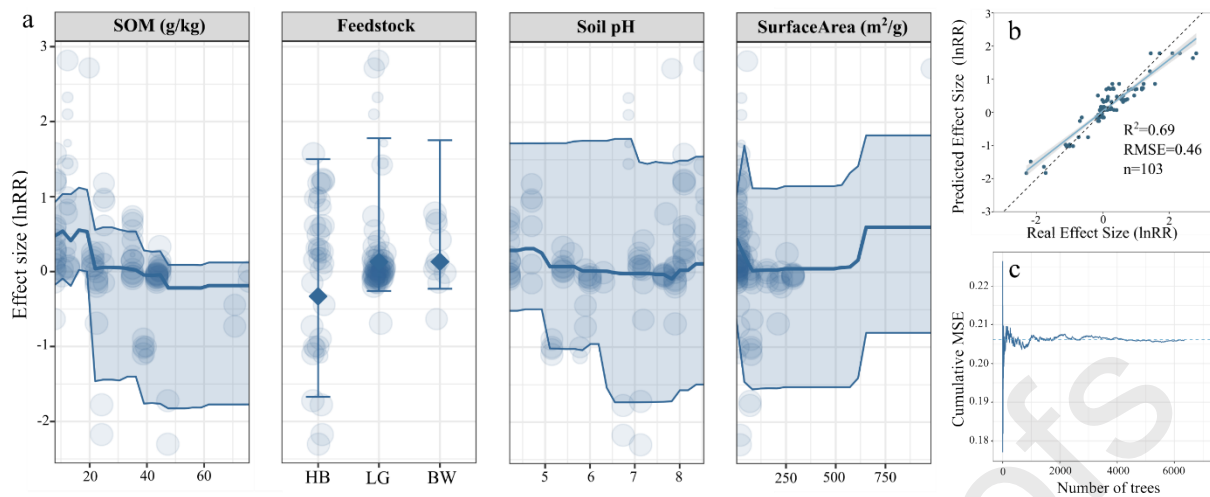


Figure 6. Partial dependence plots and validation plots. a Partial dependence plots showing the impact of biochar application on pesticide residues in soil. Each plot uses blue points to represent individual study observations, with curves showing the estimated mean effect size as a function of each parameter, and the 95% confidence intervals shaded around these curves. The plots are arranged by their importance as determined by the random forest model. For biochar feedstock materials, HB represents herbaceous material, LG stands for lignocellulosic material, and BW is a biowaste material. **b** Validation plots of all predicted effect sizes by the random forest model and real effect sizes. **c** The convergence plot of the random forest model.

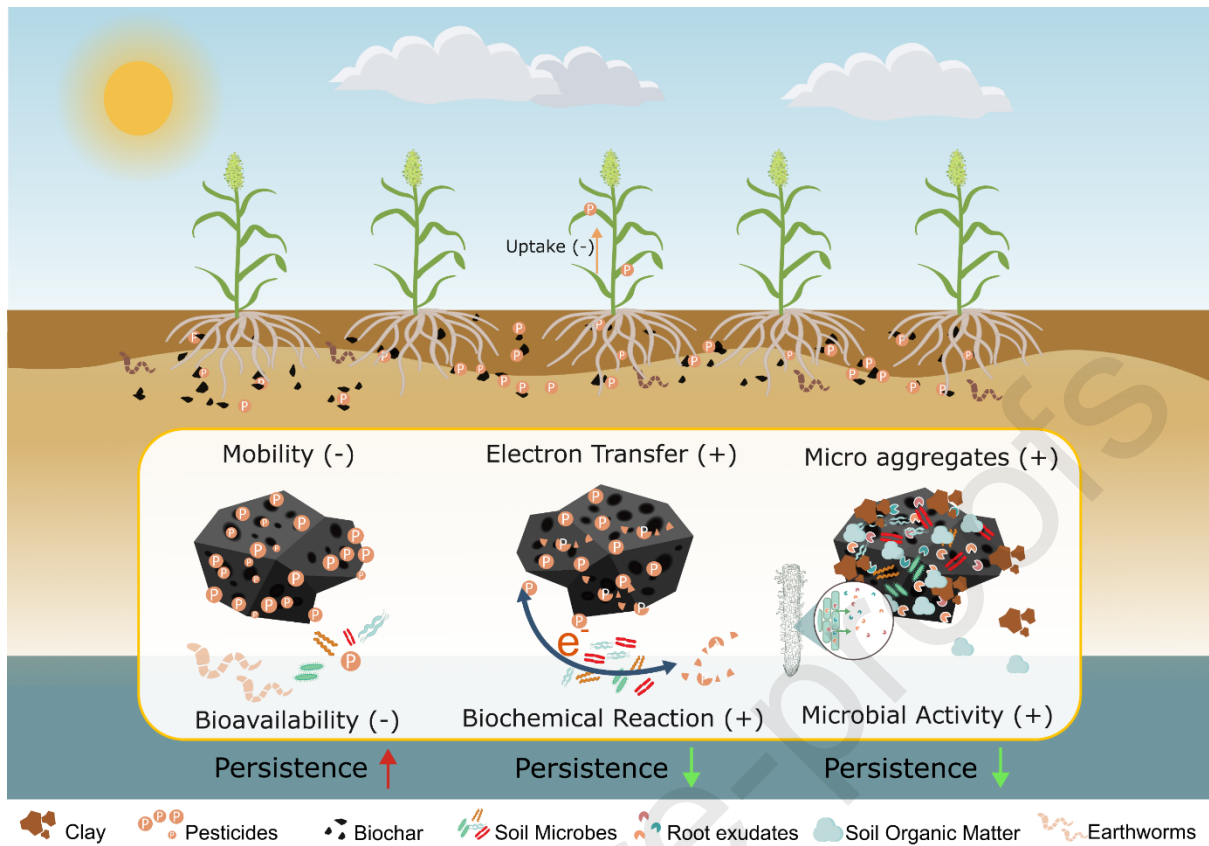


Figure 7. Biochar's dual role in pesticide (P) interactions in soil: adsorption reducing bioavailability and potential persistence (+), and electron shuttle effect due to the abundance of persistent free radicals (PFRs) enhancing biochemical reactions and microbial activities, potentially decreasing pesticide persistence (-).

Table 1. Variable groupings for pyrolysis temperature, application rate, soil pH, and soil organic matter (SOM) levels used in meta-analysis.

Variables	Group	Range
Pyrolysis temperature	Low	< 300 °C
	Medium	300-500 °C
	High	> 500 °C
Application rate	< 0.5%	
	0.5-2%	
	2-5%	
	> 5%	
Soil pH	Low	< 6
	Medium	6-8
	High	> 8
Soil organic matter (SOM)	Low	< 2%
	Medium	2-4%
	High	> 4%
Feedstock material	Lignocellulosic biomass	Wood and nutshells
	Herbaceous biomass	Herbaceous plants and straws
	Biowaste materials	Manure, sludge and food waste

Pesticide types

Triazole

Triazine

Organochlorine

Organophosphorus

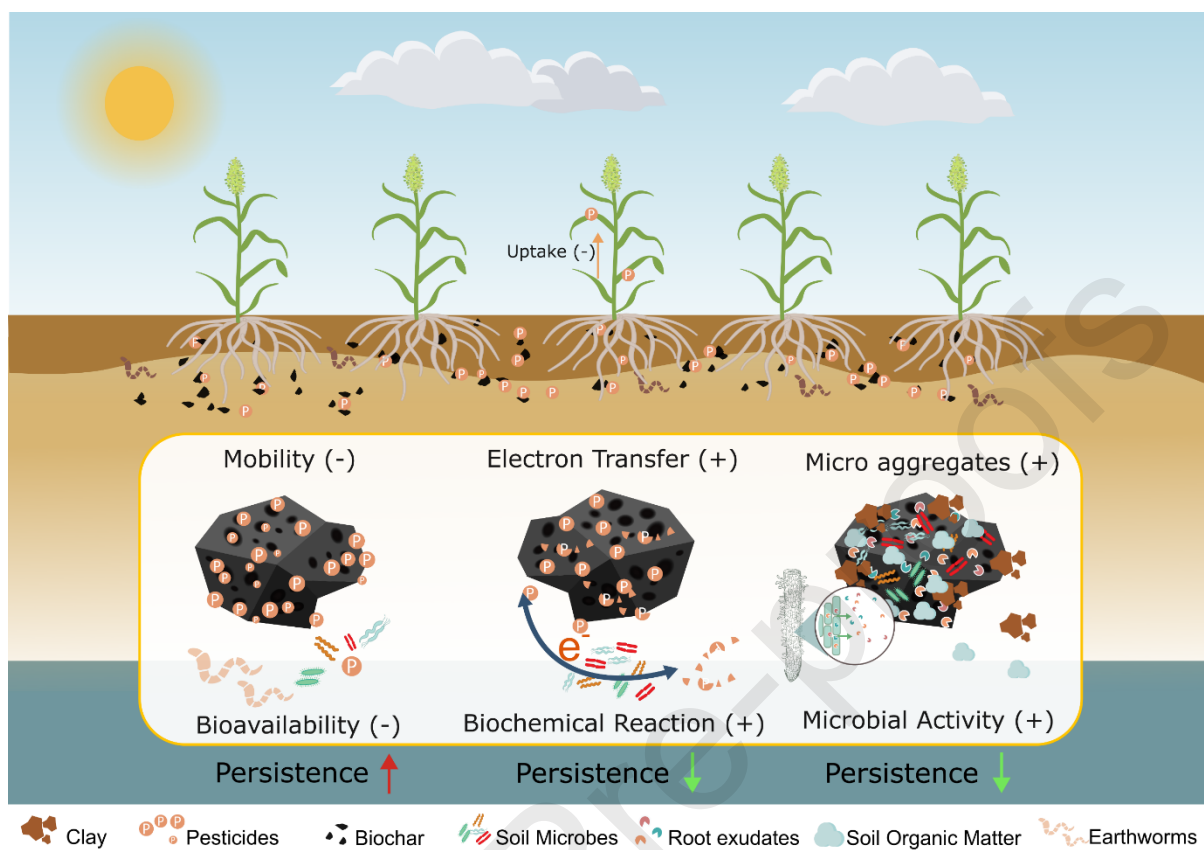
Organofluorine

Table 2. The overall effect size of biochar application on pesticide residues in soil and organisms.

	Residues in soil	Accumulation in organisms
Number of observations	245	141
Change (%)	6.01 (-25.84,37.87) %	-66.23 (-106.80, -25.65) %
<i>p-value</i> of Egger's test	0.26	0.91

The numbers in brackets represent the 95% confidence intervals for the data.

Graphic Abstract



Highlights

- Meta-analysis incorporating machine learning was used to analyze 386 observations.
- No definitive increase in soil pesticide concentrations due to the biochar application.
- A 66% reduction of pesticide within soil organisms was observed in biochar-amended soil.
- Soil organic matter was identified as a key factor influencing biochar-pesticide interactions.

CRedit author statement

Jingyu Wang: Conceptualization, Formal analysis, Investigation, Writing-Original draft, Visualization. **Trine Norgaard:** Supervision, Writing-reviewing and editing. **Lorenzo Pugliese:** Writing-reviewing and editing. **Pedro N. Carvalho:** Writing-reviewing and editing. **Shubiao Wu:** Funding acquisition, Conceptualization, Supervision, Writing-reviewing and editing.

Declaration of interests

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.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: