

Responses to the comments from Reviewer

Reviewer #1

Comment 1: The references cited in the MS are relatively dated. It is recommended that the authors incorporate more recently published relevant literature to strengthen the timeliness of the review.

Response: Thank you for this insightful comment. We have added recently published literature. We believe that these revisions improve both the timeliness and theoretical grounding of the manuscript.

Comment 2: It is recommended that the detailed calculations pertaining to the electrochemical performance and soil internal forces be provided in the Supporting Information.

Response: Thank you for this valuable comment. We have included detailed calculations related to the electrochemical properties of the soil surface and soil internal forces to enhance the transparency and reproducibility of the methodology.

1. Calculation of soil surface electrochemical properties

The calculation formula for parameters related to the electrochemical properties of the soil surface is as follows:

a. Surface potential φ_0 :

$$\varphi_0 = \frac{2RT}{2(\beta_{Ca} - \beta_{Na})F} \ln \frac{a_{Ca}^0 N_{Na}}{a_{Na}^0 N_{Ca}} \quad (1)$$

where φ_0 (V) is the surface potential; R ($J K^{-1} mol^{-1}$) is the ideal gas constant; T (K) is the absolute temperature; F ($C mol^{-1}$) is the Faraday constant; β_{Ca} and β_{Na} are the effective charge coefficients of Ca^{2+} and Na^{+} , respectively, with $\beta_{Ca} = -0.0213 \ln(I^{0.5})$

+ 1.2331 and $\beta_{Na} = 0.0213\ln(I^{0.5}) + 0.766$; I (mol L⁻¹) is the ionic strength; a_{Na}^0 (mol L⁻¹) and a_{Ca}^0 (mol L⁻¹) are the activities of Na⁺ and Ca²⁺ in solution; and N_{Na} (mol g⁻¹) and N_{Ca} (mol g⁻¹) are the amounts of Na⁺ and Ca²⁺ adsorbed by the soil.

b. Surface charge density σ_0 :

$$\sigma_0 = \text{sgn}(\varphi_0) \sqrt{\frac{\varepsilon RT}{2\pi} \left(a_{Na}^0 e^{\frac{\beta_{Na} F \varphi_0}{RT}} + a_{Ca}^0 e^{\frac{2\beta_{Ca} F \varphi_0}{RT}} \right)} \quad (2)$$

In the equation: σ_0 (C m⁻²) is the surface charge density of soil particles; ε is the dielectric constant of water, with a value of 8.9×10^{-10} C² J⁻¹ dm⁻¹.

c. Surface electric field strength E_0 :

$$E_0 = \frac{4\pi}{\varepsilon} \sigma_0 \quad (3)$$

In the equation: E_0 (V m⁻¹) is the surface electric field strength.

d. Specific surface area S :

$$S = \frac{N_{Na} \kappa}{m a_{Na}^0} e^{\frac{\beta_{Na} F \varphi_0}{2RT}} = \frac{N_{Ca} \kappa}{m a_{Ca}^0} e^{\frac{\beta_{Ca} F \varphi_0}{RT}} \quad (4)$$

In the equation: S (m² g⁻¹) is the specific surface area; $m = 0.5259\ln(c_{Na}^0/c_{Ca}^0) + 1.992$; κ (dm⁻¹) is the Debye parameter, and its reciprocal κ^{-1} represents the thickness of the diffusion double layer of colloidal particles, calculated as follows:

$$\kappa = \sqrt{\frac{8\pi F^2 C_0}{\varepsilon RT}} \quad (5)$$

e. Surface charge number (SCN):

$$SCN = 10^5 \frac{S \sigma_0}{F} \quad (6)$$

In the equation: SCN (cmol(c) kg⁻¹) is the surface charge number.

2. Calculation of soil internal forces

The SIF interactions between soil particles at the mesoscopic scale mainly include electrostatic repulsive pressure (P_E), surface hydration repulsive pressure (P_h), and van der Waals attractive pressure (P_{vdw}). The net inter-particle force (P_{net}) is the combined force of the three, which can be calculated from the soil surface property parameter to obtain the SIFs, calculated as follows.

Electrostatic repulsive pressure (P_E)

$$P_E = \frac{2}{101} RTc_0 \left\{ \cosh \left[\frac{ZF\phi(d/2)}{RT} \right] - 1 \right\} \quad (7)$$

Where P_E (atm) is the electrostatic repulsive pressure; c_0 (mol L⁻¹) denotes the concentration of ions in the native solution; d (dm) is the distance between neighboring particles; ϕ (d/2) (V) is the midpoint potential at the overlap of the particle bilayers; and Z denotes the valence of the cation.

Surface hydration repulsive pressure (P_h)

$$P_h = 3.33 \times 10^4 e^{-5.76 \times 10^9 d} \quad (8)$$

Where P_h (atm) is the surface hydration repulsive pressure; d (dm) denotes the distance from the particle surface.

Van der Waals attractive pressure (P_{vdw})

$$P_{vdw} = -\frac{A_{eff}}{0.6\pi} (10d)^{-3} \quad (9)$$

Where P_{vdw} (atm) is van der Waals attractive pressure; A_{eff} (J) is Hamaker constant.

Hamaker constant was determined using the method proposed by Tuller and Or. (2005). Weigh 10 g of soil samples sieved through a 2 mm mesh and place them in an aluminum box. Add varying volumes of water to the samples, mix thoroughly, seal

with plastic film, and allow them to equilibrate for one week. Soil water potential at different moisture contents was measured using a dew point water potential meter (WP4-T). The samples were then weighed, dried at 105 °C, and re-weighed to calculate the soil water content. Hamaker constant was obtained by fitting the soil water potential to the water content through the following model.

$$\theta_m = -\rho_w S \left(\sqrt[3]{\frac{A_{\text{eff}}}{6\pi\rho_w g\psi}} \right) \quad (10)$$

Where θ_m (kg kg⁻¹) is the soil water content; ρ_w (kg m⁻³) is the density of water; S (m² g⁻¹) is the SSA of the soil; A_{eff} (J) is the Hamaker constant; and g (m s⁻²) is the acceleration of gravity; ψ (m H₂O) is the soil water potential.

Net force (P_{net}):

$$P_{\text{net}} = P_E + P_h + P_{\text{vdw}} \quad (11)$$

Comment 3: Soil electrochemical properties under biochar treatment for 365 days?

Response: Thank you very much for this helpful comment. The soil electrochemical properties under biochar treatment for 365 days have been provided in the Supporting Information as Supplementary Table S1.

Comment 4: The data in Table 5 should be used the same order of magnitude.

Response: Thank you very much for this helpful suggestion. We have standardized all Hamaker constants in Table 5 to the same order of magnitude, namely $\times 10^{-20}$ J.

Comment 5: Fig. 9, the differences between a and b, c and d?

Response: Thank you very much for this helpful comment. In the revised manuscript, we have clarified the differences among Fig. 9a–d in the figure caption. Specifically, Fig. 9a shows the relationship between soil aggregate breaking strength and net

interparticle pressure for the $< 5 \mu\text{m}$ and $< 10 \mu\text{m}$ particle fractions at a separation distance of 2 nm under different maize straw biochar application rates after 180 days. Fig. 9b shows the corresponding relationship under different wheat straw biochar application rates after 180 days. Fig. 9c shows the relationship for maize straw biochar after 365 days, while Fig. 9d shows the relationship for wheat straw biochar after 365 days. We have revised the caption accordingly to make the figure easier to understand.

Reviewer #2

This manuscript investigates the effects of maize straw biochar and wheat straw biochar on soil aggregate stability by linking active organic carbon fractions, soil surface electrochemical properties, soil internal forces, and aggregate breakdown behavior. The study provides valuable insights into the mechanisms underlying biochar-induced soil structural improvement. The combination of organic carbon fraction analysis and quantitative evaluation of soil internal forces represents a meaningful contribution to the field of soil physics and soil amendment research. However, several issues regarding methodological clarification, mechanistic interpretation, and presentation should be addressed to further improve the manuscript. Therefore, I recommend **minor revision** before publication.

1. The calculation of internal soil forces is a key innovation of this study. Specific details regarding this theoretical calculation should be provided.

Response: Thank you for this valuable comment. We have added detailed calculation procedures for soil particle interaction forces.

2. The authors used Na^+ -saturated soil samples to quantify aggregate stability and internal forces. Please discuss how this treatment may differ from natural soil conditions and how it affects the interpretation of the results.

Response: Thank you for this valuable comment. We agree that Na^+ saturation

represents a simplified experimental condition that differs from the complex ionic environment of natural soils. In natural soils, exchangeable cations such as Ca^{2+} , Mg^{2+} , K^{+} , and Na^{+} coexist, and their combined effects on ionic strength, electrical double-layer characteristics, and particle interactions may influence soil aggregate stability.

In this study, Na^{+} saturation was employed to minimize the interference caused by heterogeneous exchangeable cations and to provide a relatively controlled system for quantitatively evaluating the intrinsic relationship between soil internal forces (SIFs) and aggregate stability. Previous studies have shown that the polarization of Na^{+} at the soil-colloid interface is very weak; therefore, it can be used to evaluate the effect of soil internal forces on aggregate stability. Therefore, the results obtained under this condition mainly reflect the mechanisms by which biochar-induced changes in soil surface properties regulate interparticle forces and aggregate stability, rather than directly representing all processes occurring under field conditions.

We have revised the Discussion and Conclusions sections to explicitly acknowledge this limitation. We further clarified that the quantitative estimation of SIFs under Na^{+} -saturated conditions provides mechanistic insights into biochar-induced structural changes, but the magnitude of these effects may vary under natural soil environments with diverse electrolyte compositions. Future studies involving mixed electrolyte systems, different soil types, and long-term field validation are needed to evaluate the broader applicability of this mechanism.

Please refer to lines 529–540, 551–555.

3. This paper emphasizes that biochar enhances agglomerate stability by strengthening van der Waals forces and weakening electrostatic repulsions. However, the role of hydration repulsions appears to be rarely mentioned. Please explain why hydration repulsions are neglected.

Response: Thank you for this valuable comment. In fact, hydration repulsion was incorporated into our quantitative estimation of soil internal forces. However, our discussion mainly focused on van der Waals attraction and electrostatic repulsion

because these two forces exhibited the most pronounced changes in response to biochar addition. Biochar increased soil specific surface area, surface charge number, and the Hamaker constant, thereby enhancing van der Waals attractive pressure and modifying electrostatic interactions between soil particles. In contrast, hydration repulsion is primarily governed by interparticle distance and is only weakly affected by biochar-induced changes in surface properties (Figure 6). Therefore, hydration repulsion was incorporated into the calculation of soil internal forces rather than neglected.

4. Since soil electrolyte concentration varies substantially under different irrigation, salinity, and climate conditions, the authors should clarify how the laboratory electrolyte gradient relates to realistic soil environments.

Response: Thank you for this valuable comment. We appreciate the reviewer's valuable comment regarding the relationship between the laboratory electrolyte gradient and realistic soil environments. We agree that electrolyte concentrations in natural soils can vary substantially depending on irrigation practices, salinity conditions, climatic factors, and soil properties. Therefore, the electrolyte concentrations used in this study should not be interpreted as direct representations of all field soil solution conditions.

The primary objective of establishing a broad electrolyte concentration gradient was to provide a controlled experimental framework for quantifying the response of soil particle interactions under different ionic environments. By systematically modifying electrolyte concentration, we aimed to regulate the surface electrochemical conditions of soil particles and evaluate how changes in interparticle forces, including electrostatic repulsion, hydration repulsion, and van der Waals attraction, contribute to aggregate stability. In this context, the selected concentration range was designed mainly for mechanistic exploration rather than direct simulation of a specific field scenario. Some concentrations used in the laboratory experiments may exceed those commonly encountered in natural soils. Nevertheless, these controlled gradients allow the identification of critical changes in particle interaction forces and provide

quantitative insights into the mechanisms controlling soil aggregate stability.

5. Natural soils typically contain a variety of exchangeable cations and a complex electrolyte composition. The limitations of the experimental design in this study should be discussed in greater detail, and future research directions involving mixed electrolyte systems or field validation should be proposed.

Response: Thank you for your suggestion. See Comment 2 for the relevant response.