

REVIEW

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Biochar as a rhizosphere interface engineer: integrated regulation of microenvironments, biogeochemical cycling, and plant resilience

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Abstract

Biochar acts as a rhizosphere interface engineer, reshaping physical, chemical, and biological gradients across the root–soil–microorganism continuum. Physically, it enhances aggregation by 13.9–18.9% and increases porosity by 8.2–41.6%, improving root penetration and creating microbial refuges. Chemically, its functional groups buffer rhizosphere pH, adsorb root-derived organic acids, and mediate redox reactions that govern nutrient speciation and contaminant immobilization. Biologically, it provides protected microhabitats, enriches functional taxa, and stimulates enzyme activities. On average, urease activity rises by 23.1%, alkaline phosphatase by 25.4%, and nitrogen-cycling genes *amoA* and *nosZ* increase by 25.3% and 17.0%, respectively. These functional pathways are mechanistically coupled and shift with soil conditions. Enhanced pore connectivity promotes oxygen diffusion toward roots, driving iron redox cycling and iron plaque formation, which modulates phosphorus solubility and selects for microbial consortia coupling nitrogen transformation to iron reduction. The relative importance of these mechanisms varies by context: physical water retention dominates in coarse-textured soils under drought, pH buffering and sorption prevail in acidic soils, and microbial habitat effects are most significant in nutrient-limited systems driven by rhizodeposits. Collectively, these alterations decrease the mineralization of indigenous soil organic carbon by an average of over 5.5%, elevate the retention of root-derived carbon in subsoil by 20% on average, and lower nitrogen leaching by 10.9%. Meanwhile, plant stress resistance is improved via optimized rhizosphere microbial communities and enhanced rhizosphere signal transduction. Translating these benefits into practice requires matching biochar properties to specific soil conditions. For alkaline sandy loam soils, wood- or crop residue-derived biochar produced above 500 °C, applied at 20–40 t ha⁻¹ with 0.5–2 mm particles, is optimal. Acidic soils, however, require lower application rates of 5–25 t ha⁻¹. Particles smaller than 0.5 mm, as well as sludge- or manure-derived biochar produced below 500 °C, should be avoided without prior ecotoxicological screening mainly due to the risk of its transport or cotransport with contaminants. Long-term efficacy depends on repeated moderate-rate applications to manage aging-related decline and nutrient imbalances. Future research should resolve context-dependent contradictions through systematic dose–response experiments, define safe application windows by tracking aging trajectories, and reconcile conflicting microbial responses using field-based metatranscriptomics paired with enzyme assays.

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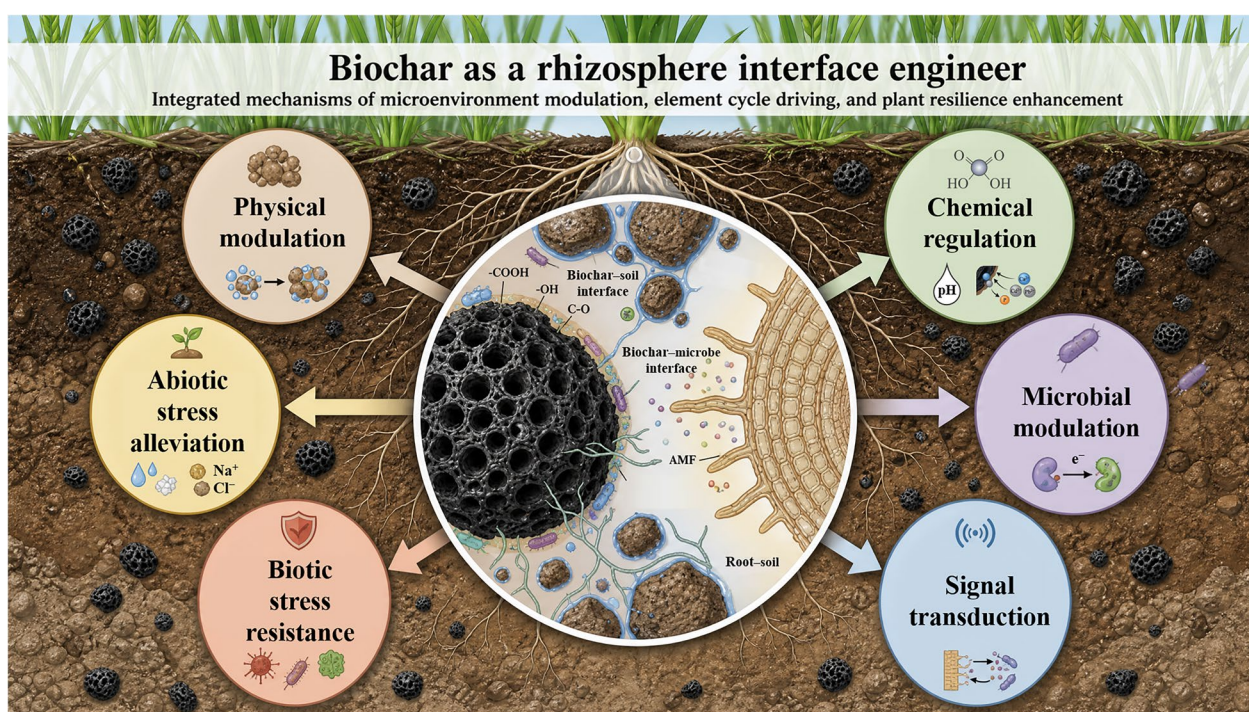
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Highlights

- Biochar acts as a rhizosphere interface engineer, regulating root–soil–microbe systems through combined multi-pathways.
- These changes cut soil carbon and nitrogen losses, boost nutrient retention, and enhance plant stress resilience.
- Matching biochar to local soil conditions maximizes agronomic benefits and mitigates environmental risks.

Keywords Biochar, Rhizosphere, Biogeochemical processes, Elemental cycles, Ecological functions

Graphical Abstract



1 Introduction

The rhizosphere, a narrow yet dynamic soil zone extending millimeters to centimeters from the root surface, represents a critical interface where plants, soil, and microorganisms engage in intense biogeochemical interactions (Jia et al. 2023; Kuzyakov And Razavi 2019; Li et al. 2025b; Zhang et al. 2021). This hotspot is functionally distinct from bulk soil, driven by continuous inputs of root exudates (organic acids, amino acids, and sugars) that alter local pH and redox conditions to mobilize poorly soluble nutrients like phosphorus, potassium, and iron. These labile carbon inputs not only accelerate microbial metabolism and contribute to microbial biomass accumulation but also exert a strong regulatory effect on native soil organic carbon (SOC) turnover

through priming effects (Bölscher et al. 2025; Mueller et al. 2024). Beyond nutrient cycling, rhizosphere processes enhance plant fitness via symbioses and pathogen suppression, while also modulating contaminant bioavailability through adsorption and degradation (Liu et al. 2024a; Meng et al. 2024a; Mueller et al. 2024). Consequently, deciphering rhizosphere biogeochemistry is fundamental to advancing both sustainable agriculture and environmental remediation (Finzi et al. 2015).

Biochar, a carbon-rich, porous material produced from biomass pyrolysis, has emerged as a powerful soil amendment with multifaceted impacts (Lehmann 2007; Woolf et al. 2010). Its high surface area, porous architecture, and reactive functional groups enable strong interactions with soil components, water, nutrients, and

microorganisms (Liu et al. 2019; Sun et al. 2020; Wang et al. 2020). Biochar can improve soil physical structure by increasing water-holding capacity in sandy soils and alleviating compaction in clay-rich soils (Sun And Lu 2014). Biochar can directly supply and retain nutrients like ammonium and phosphate, while also ameliorating soil acidity and increasing cation exchange capacity (Hagemann et al. 2017; Luo et al. 2025). As a protected microbial habitat, biochar selectively shapes community composition by supporting beneficial taxa and suppressing certain pathogens, thereby linking its application to broader soil health outcomes (Campos et al. 2020; Paliağa et al. 2025). Furthermore, biochar serves as a carbon sequestration strategy (Deng et al. 2024; Nan et al. 2025) and an effective remediation tool for immobilizing heavy metals and organic contaminants (Guo 2024; Palansooriya et al. 2022a, 2022b). Critically, these interfacial properties are not static but evolve dynamically through field aging processes that progressively alter biochar surface chemistry, pore architecture, and interactions with the rhizosphere microbiome, with profound implications for long-term biogeochemical functioning (Mia et al. 2017; Wang et al. 2020).

The confluence of these two fields, rhizosphere science and biochar technology, has created a major research frontier, as biochar is increasingly recognized not just as a bulk soil modifier but as a potent regulator of the rhizosphere's spatial extent and functional intensity (Fang et al. 2021; Sarma et al. 2024; Shang et al. 2023). To advance beyond the conventional categorization of biochar merely as a soil amendment, a microbial habitat modifier, or a geochemical mediator, we introduce the concept of biochar as a “rhizosphere interface engineer”, a material that actively and synergistically reconfigures the physical, chemical, and biological gradients across the root–soil interface. We define interface engineering by three measurable criteria. First, physical re-engineering of pore architecture and connectivity, which governs water films, gas diffusion, and the spatial continuity of microbial microhabitats. Second, chemical re-engineering of pH, redox potential, and nutrient gradients that determine element speciation and bioavailability. Third, biological re-engineering of microbial community assembly and metabolic networks that couple carbon, nitrogen, and phosphorus cycling. For instance, biochar has been shown to accelerate the formation of micro-aggregates that physically protect SOC and to enhance the retention of root-derived carbon within stable organo-mineral fractions, directly exemplifying how physical and chemical re-engineering converge to strengthen carbon stabilization in the rhizosphere (Weng et al. 2017). Several

prior reviews have provided foundational syntheses of biochar–rhizosphere interactions (Głuszek et al. 2017), the role of biochar in promoting overall soil health and microbial ecology (Lehmann et al. 2011; Bolan et al. 2023), or its mediation of specific nutrient cycles, such as carbon and nitrogen (Craswell et al. 2021; Chen et al. 2024c; Yu et al. 2024). While invaluable, these works have typically reviewed physical, chemical, and biological effects individually, whereas a critical knowledge gap remains in the integrated, mechanistic understanding of how biochar's simultaneous and coupled physical, chemical, and biological alterations converge specifically within the rhizosphere to orchestrate its functions as a biogeochemical hotspot.

In this review, we operationalize the interface engineering framework through a structured synthesis that progresses from individual mechanisms to their integrated outcomes. Sections 2, 3 and 4 sequentially examine the physical, chemical, and biological dimensions of biochar-mediated rhizosphere re-engineering. Section 5 then demonstrates how these three dimensions converge to regulate the biogeochemical cycling of key elements (C, N, P, S, Fe, and others), including an analysis of how biochar buffers carbon and nitrogen fluxes under climatic stresses. Section 6 extends this analysis to plant-level ecological functions, examining enhanced resistance to both biotic and abiotic stresses. Section 7 evaluates the practical translation of these mechanistic insights through life cycle assessment, economic feasibility, and emerging environmental risks. Section 8 proposes a prioritized research agenda in the future. By synthesizing these coupled processes across scales, we aim to provide a mechanistic blueprint for rational biochar design and identify key research priorities for advancing sustainable agricultural ecosystems.

2 Physical modulation of the rhizosphere by biochar

The physical environment in the rhizosphere directly influences root growth and microbial activities (Korenblum et al. 2022; Kuzyakov And Razavi 2019). As shown in Fig. 1, biochar regulates this physical environment through multiple interacting pathways that originate from its pore structure and surface chemistry (Joseph et al. 2021; Schmidt et al. 2021). These responses depend on feedstock type, pyrolysis temperature, application rate, soil texture, and environmental conditions (Blanco-Canqui 2017; Wei et al. 2023), and can be either direct, through changes in the soil matrix, or indirect, via biochar-driven alterations in soil chemistry and microbial communities that feedback on aggregation and pore development (Bruun et al. 2014).

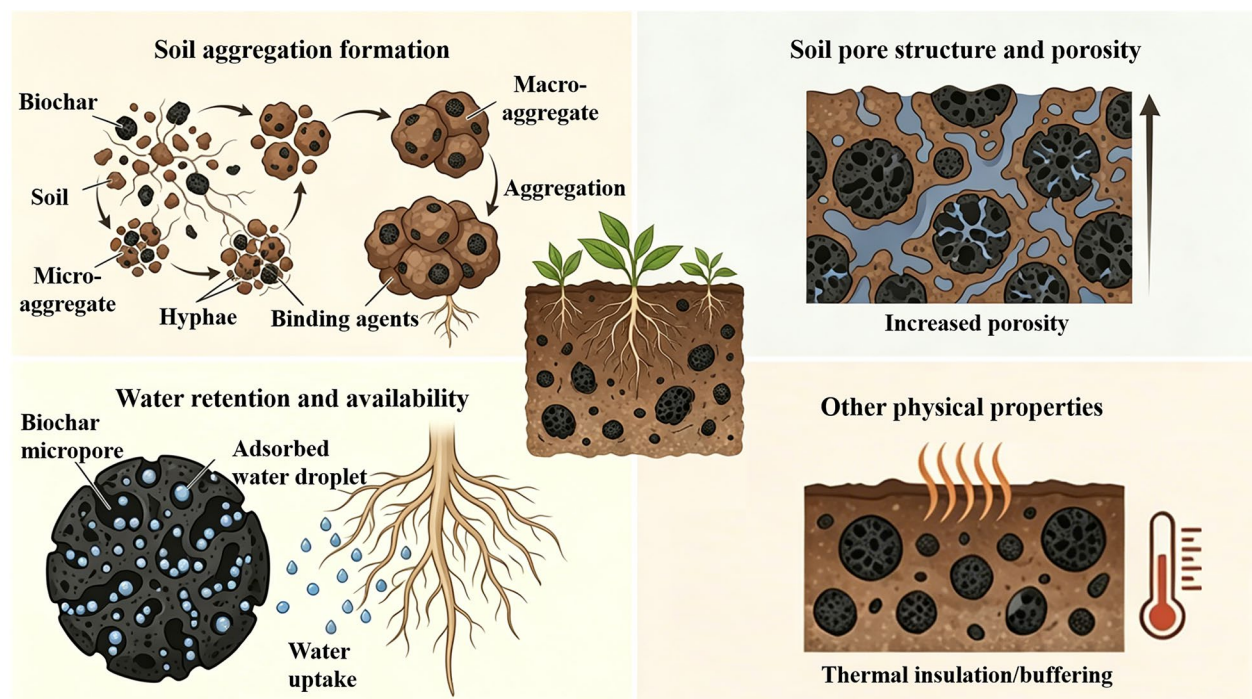


Fig. 1 Mechanisms underlying biochar-mediated regulation of rhizosphere physical environment

2.1 Soil structure, pore architecture, and root penetration

Biochar enhances soil structure primarily by improving the formation and stability of aggregates. Its porous structure, high specific surface area, and abundant functional groups facilitate bonding between cations, organic matter, and mineral particles, thereby mitigating the physical constraints on root growth imposed by soil compaction (Joseph et al. 2021). Biochar particles can act as nuclei for aggregation, providing attachment sites for microorganisms and roots, while their surfaces support the formation of organo-mineral coatings that further stabilize aggregates (Weng et al. 2017, 2022). In parallel, dissolved organic carbon released from biochar also stimulates root and microbial activity, particularly that of mycorrhizal fungi, whose exudates and hyphal networks directly drive the formation of macroaggregates from microaggregates (Bolan et al. 2023; Wen et al. 2022). The quantitative significance of these mechanisms is confirmed by a meta-analysis of 641 independent observations that reported a 13.9–18.9% increase in soil aggregate content after biochar amendment, with the magnitude varying by soil type, biochar properties, and experimental conditions (Islam et al. 2021). In fine-textured soils, application rates of approximately 20–30 t ha⁻¹ can effectively increase the proportion and stability of macroaggregates (> 2 mm), an improvement attributed to enhanced cation exchange capacity and stronger organic–mineral binding (Islam et al. 2021). For instance,

in a saline-alkaline clay loam, biochar applied at 30 t ha⁻¹ increased the fraction of >2 mm aggregates by 1.53-fold and raised the mean weight diameter, a measure of aggregate size distribution where higher values indicate greater macro-aggregation, by 26–40% (Jia et al. 2024). By contrast, in sandy loam soils with low initial organic carbon, higher application rates are generally required to achieve measurable improvements (Zhang et al. 2015, 2020). The aggregation benefits are also modulated by feedstock source and pyrolysis temperature. Woody and cereal residue biochar generally outperform straw-derived biochar, and high-temperature biochar (>600 °C) delivers more pronounced structural improvements (Islam et al. 2021).

Beyond aggregation, biochar amendment increases total soil porosity through three pathways, namely the intrinsic pore structure of biochar, the formation of inter-aggregate pores driven by macroaggregate development, and the generation of biopores associated with stimulated microbial activity and root growth. Reported increases range from 8.20% to 41.6% and depend strongly on the physicochemical properties of both soil and biochar (Jia et al. 2024). Biochar also shifts the pore size distribution, reducing the proportion of ultrafine pores while increasing the fraction of larger, well-connected pores, a change that enhances the exchange of air, water, and nutrients between aggregates and the surrounding matrix (Yu et al. 2016). Improved pore connectivity is critical because it not

only facilitates root elongation and water movement but also promotes oxygen diffusion into deeper soil layers, thereby supporting aerobic microbial metabolism and nutrient mineralization in the rhizosphere. In a saline-alkaline soil amended with 30 t ha⁻¹ biochar, the pore connectivity index, a dimensionless metric of pore network continuity, reached 2.36, reflecting substantially enhanced continuity of the pore network (Jia et al. 2024). Collectively, these findings establish a generalizable principle that biochar consistently shifts soil toward a more porous, well-aggregated state, with the magnitude of improvement governed by application rate, feedstock type, and soil texture.

It should be noted that the meta-analysis and many supporting studies cited above measure physical properties in bulk soil rather than in the millimeter-scale rhizosphere microdomain directly adjacent to root surfaces. Directly quantifying aggregation, bulk density, and pore connectivity at the rhizosphere scale remains technically challenging because of the sample volume requirements of current analytical methods and the steep spatial gradients in root exudates, water content, and microbial activity over sub-millimeter distances. In theory, the rhizosphere experiences more intense wet-dry and shrink-swell cycles, higher concentrations of microbial exudates and extracellular polymeric substances, and more frequent root-induced compaction, all of which can locally modify the physical properties reported at the bulk scale. Despite these limitations, the directional trends from bulk soil meta-analyses remain informative for the rhizosphere context because the underlying mechanisms driving aggregation and pore development, including organo-mineral binding, hyphal entanglement, particle interlocking, and microbial biofilm formation, operate in both compartments.

These structural improvements at the aggregate and pore scale translate directly into positive root responses. In a vineyard trial, biochar applied at 10 t ha⁻¹ increased the proportion of >2 mm macroaggregates and simultaneously raised fine root biomass from 8.56 to 13.3 g m⁻². The mean diameter of fine roots increased from 0.46 mm to 0.56 mm, while the turnover rate decreased from 1.02 yr⁻¹ to 0.95 yr⁻¹, indicating extended root lifespan under improved physical conditions (Amendola et al. 2017). Reduced soil bulk density, typically by 3–31%, with greater reductions in coarse-textured soils, further facilitates root penetration by creating a looser matrix (Blanco-Canqui 2017). Collectively, these interrelated changes in aggregation, pore architecture, and bulk density concurrently enhance hydraulic conductivity and oxygen availability (Głuszek et al. 2017; Jones et al. 2012; Yuan et al. 2025a).

2.2 Soil water retention and hydraulic transport

The pore modifications described above directly regulate rhizosphere water dynamics. Biochar alters pore size distribution and surface wettability, which alters the balance between capillary and non-capillary pores (Tanure et al. 2019). These changes directly modulate root water availability and constitute a core physical pathway linking biochar to root system function (Horel et al. 2019). The hydrological responses are not uniform but vary non-linearly with soil properties, biochar characteristics, and application regimes (Ramezanzadeh et al. 2023). Two global meta-analyses consistently demonstrate that biochar improves plant-available water most strongly in coarse-textured soils, with reported increases of approximately 45–51% in sand and loamy sand, around 20% in loam soils, and diminishing to negligible effects in clay soils. This pattern correlates positively with biochar specific surface area and cation exchange capacity (Razzaghi et al. 2020; Wei et al. 2023) and arises from the infilling of large interparticle pores by biochar micropores, which increases the volume of capillary pores that retain plant-available water. Field and mesocosm studies confirm significant increases in field capacity in sandy soils (Głab et al. 2016).

Biochar also modulates soil water transport. In a sandy loam field experiment, biochar mitigated drought-induced reductions in unsaturated hydraulic conductivity, with maize transpiration rates in amended plots remaining 83% higher than controls at low soil moisture (Tirgarsoltani et al. 2021). This benefit is mechanistically linked to enhanced aggregate stability, which maintains continuous hydraulically conductive pathways for water movement (Tirgarsoltani et al. 2021). Improved hydraulic conductivity simultaneously facilitates oxygen replenishment in the rhizosphere after rainfall or irrigation, helping to alleviate transient hypoxia. However, biochar does not always improve water transport. In karst sloping farmland, application rates of 30 and 60 t ha⁻¹ extended water infiltration time and reduced the average infiltration rate, likely due to strong water adsorption by hydrophilic functional groups and the partial clogging of interparticle pores by fine biochar particles (Liu et al. 2017c; Peng et al. 2026). This negative outcome was observed at very high application rates and likely reflects rate-specific pore clogging rather than a general limitation of biochar, as at rates below 20 t ha⁻¹, such adverse effects on infiltration are rarely reported, suggesting that the balance between beneficial pore modification and detrimental clogging is strongly dose-dependent. Biochar particle size further modulates these effects, particles of 1 to 2 mm typically improve field capacity more effectively than particles smaller than 1 mm, whereas particles larger than 2 mm show no consistent advantage in available

datasets. Contrary to common assumptions, fine biochar does not enhance field capacity through higher specific surface area alone and may even reduce soil water retention due to pore clogging (Table S1). Additionally, fresh unaged biochar can temporarily reduce water infiltration owing to surface hydrophobicity (HC), but natural aging and surface oxidation progressively increase hydrophilicity, leading to sustained improvements in water retention over time (Baronti et al. 2022; Razzaghi et al. 2020). Taken together, these findings indicate that biochar enhances rhizosphere water availability when applied at moderate rates to coarse-textured soils using aged biochar with appropriate particle size, whereas high application rates, fine particles, and fresh hydrophobic biochar can transiently impair infiltration or cause pore clogging. This underscores the need to match biochar properties to soil hydrological constraints.

Empirical evidence consistently demonstrates that biochar amendment enhances plant-available water and resilience to soil moisture deficits. In a pot experiment with compacted urban soil, biochar significantly increased the proportion of macroaggregates > 250 μm , improved aeration and drainage under wet-dry cycles, and increased ginkgo seedling biomass by 369% (Yoo et al. 2020). In a 10-year vineyard trial, a cumulative biochar application of 44 t ha^{-1} maintained significantly higher soil water content during summer drought and increased grapevine predawn leaf water potential by 42%. The concurrent decrease in fine root biomass in the topsoil was interpreted as reduced need for extensive root foraging due to more reliable water access (Baronti et al. 2022). In degraded saline-alkaline wasteland, a biochar interlayer at 40 cm depth increased soil water content in the 0–50 cm layer by 5–21%, reduced salinity in the 0–40 cm rooting zone by 14–41%, and increased total plant biomass by 66% (Xu et al. 2025).

2.3 Thermal and mechanical properties, and electrical conductivity

In addition to altering soil structure and water dynamics, biochar modulates soil electrical conductivity, mechanical behavior, and thermal regime (Dahlawi et al. 2018). In salt-affected soils, the high cation adsorption capacity of biochar can immobilize dissolved salts, thereby reducing soil solution salinity and alleviating salt stress (Wang et al. 2024b), which in turn protects root cell membranes from osmotic damage and sustains root water uptake capacity. However, biochar can also contain soluble salts and ash, and high application rates of certain biochar may temporarily increase electrical conductivity (Mavi et al. 2022). The balance between these opposing effects is primarily governed by feedstock type and application

rate. Manure-derived biochar and those produced from halophytic feedstocks carry substantially higher ash and soluble salt loads than wood-derived biochar, and their application to already saline soils at rates exceeding 20 t ha^{-1} poses a measurable risk of exacerbating salinity stress. Conversely, wood-derived biochar produced at moderate to high temperatures typically contains low ash content and is unlikely to elevate soil electrical conductivity even at higher application rates. For crop residue biochar, the risk is intermediate and can be managed by washing biochar before application or by selecting feedstocks grown on non-saline soils. In practice, the salinity risk is most acute when high-ash biochar is applied at high rates to coarse-textured saline soils with limited leaching capacity, because the salt input from biochar can overwhelm its simultaneous capacity to adsorb and immobilize soil salts. A simple precaution is to screen biochar ash content and electrical conductivity before field application, particularly when using manure-derived biochar or applying to salt-sensitive crops.

Beyond its effects on salinity, biochar amendment also reduces soil compactness and shear strength by disrupting the close packing of mineral particles, increasing elasticity and plasticity, and lowering susceptibility to compaction under traffic loads (Blanco-Canqui 2017; Li et al. 2025a; Wang et al. 2019a), thereby reducing the mechanical impedance encountered by elongating root tips and promoting deeper root penetration. Changes in soil plasticity indices such as liquid and plastic limits have been widely documented, supporting the premise that biochar can shift mechanical properties toward a state more favorable for root penetration (Arthur et al. 2019). Biochar further influences soil thermal dynamics through its dark color, which reduces surface albedo, altering diurnal temperature fluctuations and vertical heat distribution (Bhat et al. 2022). The resulting thermal buffering can protect roots from extreme temperature stress while sustaining microbial metabolic activity in the rhizosphere. Concurrently, changes in water holding capacity and pore size distribution modulate evaporation at the soil–atmosphere interface (Chen et al. 2018; Feng et al. 2023). These thermal and hydrological changes can involve trade-offs: soil warming and altered evaporation may reduce topsoil water content under certain management practices such as ridge tillage, even when other physical properties are improved (Meng et al. 2020; Puspanathan et al. 2022). Overall, biochar-induced reductions in soil strength and salinity, together with moderated temperature fluctuations, create a physically more hospitable rhizosphere environment for root growth and microbial processes, although the net benefit depends strongly on feedstock selection and application management.

2.4 Practical considerations regarding application rates

The physical effects described in Sects. 2.1, 2.2, and 2.3 exhibit strong nonlinearity and context dependence, which has created inconsistent conclusions across studies and limited the translation of research findings into standardized field practices. Soil texture and pH represent the primary overarching controls on biochar performance because they determine the fundamental physical limitation that biochar can address. In alkaline sandy loam soils, biochar primarily improves water retention by filling large interparticle voids that characterize coarse-textured substrates. Table 1 shows that 0.5 to 2 mm biochar applied at 20 to 40 t ha⁻¹ produces the greatest benefits in these soils, with expected yield increases ranging from 50 to 166%. In acidic sandy loam soils, the optimal application range shifts to 5 to 25 t ha⁻¹ with positive effects detectable at rates as low as 2.5 t ha⁻¹ and rates exceeding 50 t ha⁻¹ not recommended. In fine-textured soils, biochar primarily enhances aggregation and reduces compaction by acting as physical anchors for organo-mineral complexes and disrupting the dense packing of clay particles. For alkaline clay loam soils, the optimal range is 20 to 40 t ha⁻¹ with positive effects beginning at 20 t ha⁻¹ and rates exceeding 40 t ha⁻¹ increasing the risk of pore clogging. For acidic silt loam soils, the optimal range is 5 to 20 t ha⁻¹ with positive effects appearing at 2 t ha⁻¹ and no significant negative effects observed across the tested rate range.

Application rate functions as the second-order control that modulates the magnitude and direction of biochar effects. Rates below the positive effect threshold rarely produce measurable changes in soil physical properties, while rates between the positive threshold and the negative risk threshold generally deliver consistent beneficial effects. Rates exceeding the negative risk threshold frequently trigger adverse outcomes including pore clogging, increased salinity, and excessive alkalinity. This pattern is consistently observed across all soil types

included in Table 1. Marginal benefits decline sharply beyond the optimal rate range and most studies show no statistically significant yield gains once rates exceed the context-specific upper limit, indicating that moderate application rates typically provide the best balance between agronomic benefit and economic cost.

Biochar particle size introduces a third-order control that modulates the balance between beneficial pore modification and detrimental pore clogging. Table 1 provides clear quantitative guidance on particle size selection and shows that particles smaller than 0.5 mm are not recommended for alkaline sandy loam soils as they produce yield reductions of 13% to 27% even at moderate application rates. Particles of 0.5 to 2 mm deliver superior overall performance across most soil types and produce expected yield increases of 13% to 101% in soils with unspecified texture, while particles smaller than 0.5 mm or larger than 2.8 mm carry elevated risk of negative effects.

Aging acts as a time-dependent fourth-order control. Fresh biochar often exhibits surface hydrophobicity that can temporarily reduce water infiltration, but natural weathering and surface oxidation progressively increase hydrophilicity over time. Aging also generates additional oxygen-containing functional groups that strengthen organo-mineral bonding and further stabilize aggregates, meaning that the full physical benefits of biochar amendment develop gradually over several years. Future research should investigate lower rate strategies combined with targeted rhizosphere placement that may deliver comparable physical improvements at a fraction of the cost.

3 Chemical modulation of rhizosphere processes by biochar

As a multifunctional soil amendment, biochar reshapes the rhizosphere chemical environment through its inherent physicochemical properties (Omokaro et al. 2025). It

Table 1 Dose–effect threshold matrix for biochar application across soil types, pH, and particle sizes (data summarized from Table S1)

Soil texture	Soil pH	Biochar particle size (mm)	Recommended rate (t ha ⁻¹)	Expected yield change (%)	Positive threshold (t ha ⁻¹)	Negative effect risk
Sandy loam	Alkaline	0.5–2	20–40	+ 50 to + 166	10	Rate > 60 t ha ⁻¹
		< 0.5	Not recommended	– 27 to – 13 (at 10 t ha ⁻¹)	None	Size < 0.5 mm
Clay loam	Acidic	< 2	5–25	+ 10 to + 30	2.5 ⁵	Rate > 50 t ha ⁻¹
		< 2	20–40	+ 96 to + 105	20	Rate > 40 t ha ⁻¹
Silt loam	Acidic	< 2	5–20	+ 20 to + 50	2	Not observed
Silty clay	Neutral	< 2	20–30	+ 33 to + 36	25	Rate > 50 t ha ⁻¹
Not specified	Neutral	0.5–2	10–20	+ 13 to + 101	10	Size < 0.5 mm or > 2.8 mm

supplies ash-borne macroelements (N, P, K) that replenish soil nutrient pools, especially in nutrient-limited soils or during peak crop nutrient demand (Singh et al. 2022). Its abundant surface OCFGs enhance nutrient retention via cation exchange and complexation, while mitigating phytotoxicity from heavy metals and organic

pollutants (Chi et al. 2024; Omokaro et al. 2025). As shown in Figs. 2, 3, 4, and 5, biochar acts as a reactive sorption reservoir and core biogeochemical interface in the rhizosphere, driving coupled processes including acid–base buffering, adsorption–desorption, complexation–precipitation, and redox reactions (Gao et al. 2021).

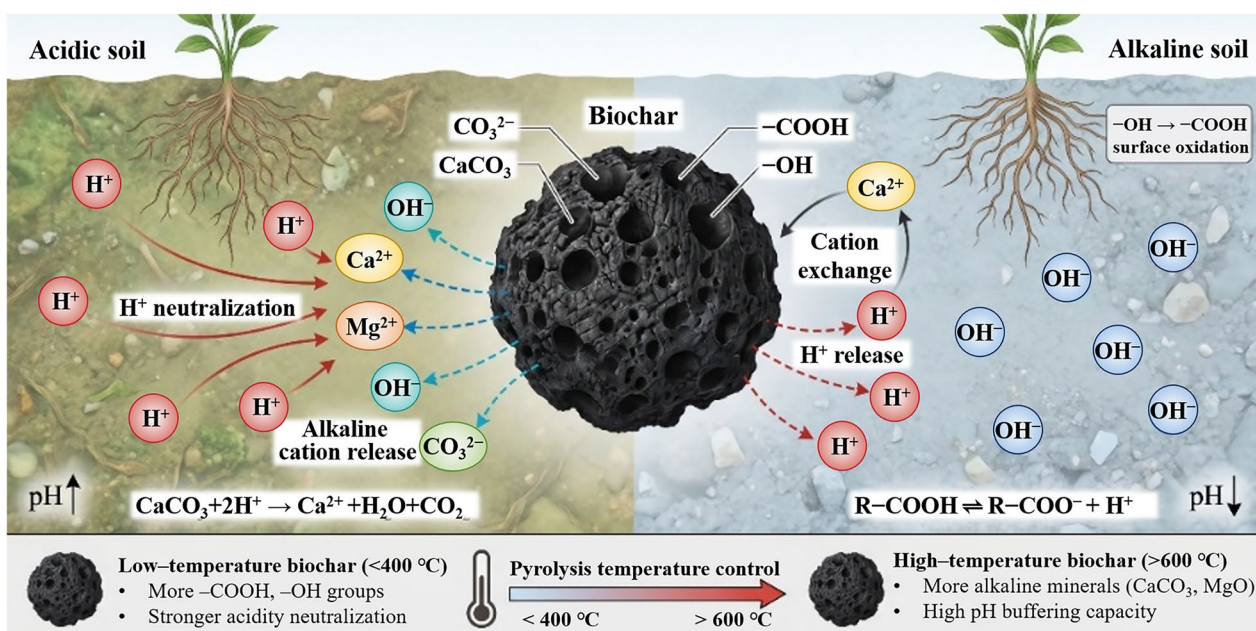


Fig. 2 Mechanisms underlying biochar-mediated regulation of rhizosphere acid–base buffering

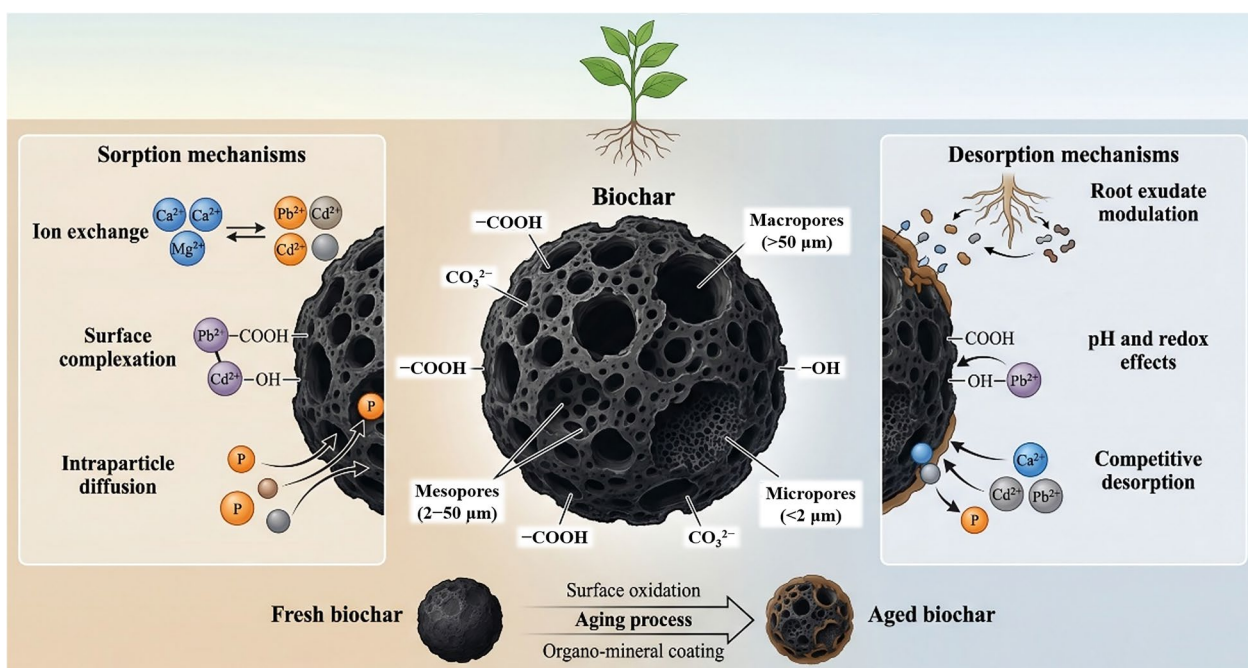


Fig. 3 Mechanisms underlying biochar-mediated regulation of rhizosphere sorption and desorption processes

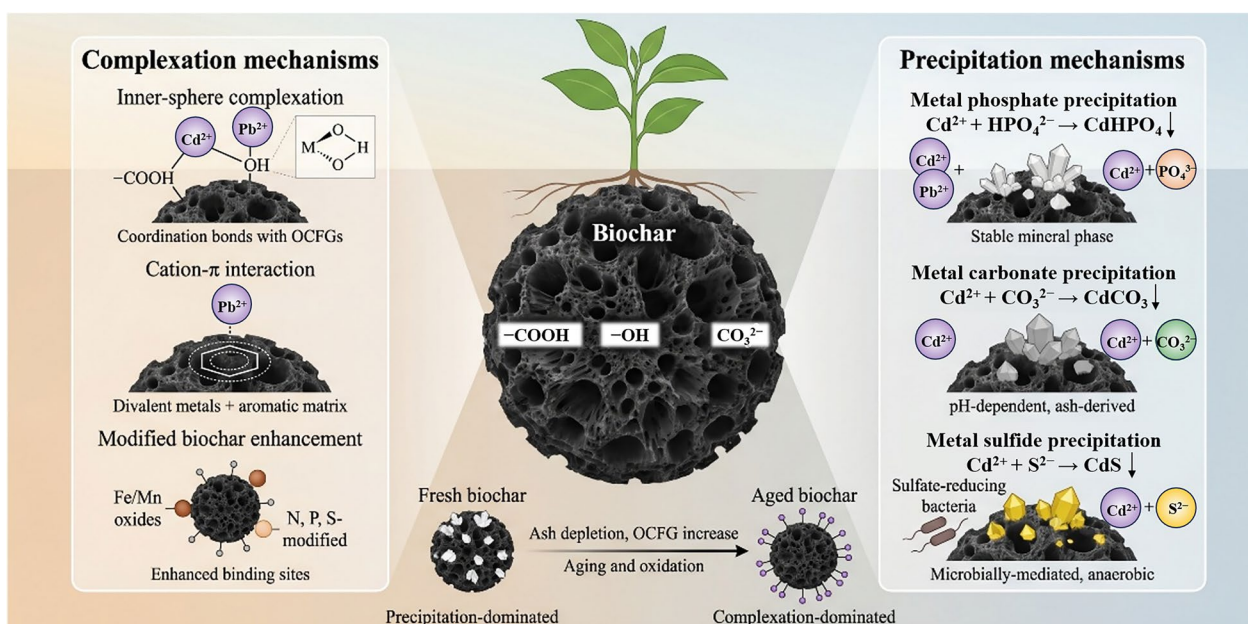


Fig. 4 Mechanisms underlying biochar-mediated regulation of rhizosphere complexation and precipitation processes

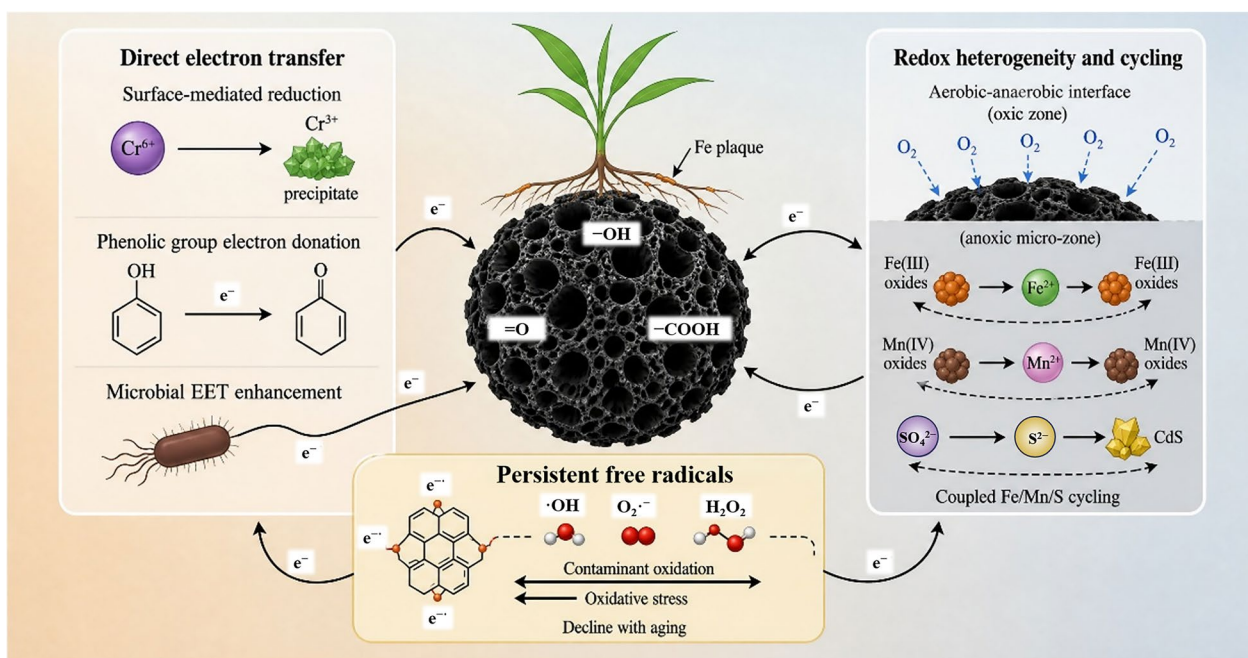


Fig. 5 Mechanisms underlying biochar-mediated regulation of rhizosphere redox and electron transfer processes

These interfacial processes mediate dynamic interactions between biochar, plant roots, and rhizosphere microorganisms, regulating elemental biogeochemical cycling, pollutant transformation and detoxification, and the overall ecological function of the rhizosphere microenvironment (Li et al. 2020; Ni et al. 2021; Yang et al. 2025a).

3.1 Acid–base buffering

Rhizosphere pH is a master variable governing nutrient bioavailability, heavy metal mobility, and rhizosphere microbial community assembly and activity (Sugihara et al. 2016). As shown in Fig. 2, biochar-driven pH changes arise from two core pathways, namely direct

proton neutralization by surface functional groups and the release of exchangeable alkaline cations via cation exchange reactions (Liu et al. 2024b; Wijitkosum 2022). The direction and magnitude of these effects are co-determined by biochar intrinsic properties and soil physicochemical characteristics, with pyrolysis temperature (here defined as low < 400 °C and high > 600 °C) exerting a more dominant control than feedstock type, because increasing pyrolysis temperature progressively eliminates acidic functional groups while enriching alkaline mineral salts, resulting in biochar products with a wide pH range of typically 5.43 to 10.8 (Zhao et al. 2013a). In acidic soils, alkaline biochar neutralizes soil protons via release of carbonate, oxide, and hydroxide minerals, with an acid-neutralizing capacity equivalent to up to one-third of agricultural lime in some scenarios (Joseph et al. 2021). Conversely, low-temperature biochar retains more acidic functional groups, and progressive surface oxidation during field aging further generates carboxylic acid groups, driving pH reduction in alkaline soils via cation exchange and carbonate-associated reactions (Joseph et al. 2010; Wijitkosum 2022).

Feedstock type also shapes the pH and liming potential of biochar, as woody residue-derived biochar generally has lower alkalinity than that produced from certain agricultural wastes, while high-temperature pyrolyzed sewage sludge biochar is typically strongly alkaline (Dimitriadou et al. 2025; Wijitkosum 2022; Zhao et al. 2013a). Engineered modified biochar can further enhance pH regulation capacity, for example, magnesium-modified biochar increased acidic soil pH from 5.67 to 6.87–6.94 at 0.5–2% application rates, outperforming unmodified biochar (Dimitriadou et al. 2025; Liu et al. 2024b). Soil type is a key determinant of these regulatory effects, as calcareous soils with strong native buffering capacity show negligible pH changes after biochar amendment, while acidic highly weathered soils exhibit significant pH elevation and enhanced cation exchange capacity (CEC) (Van Zwieten et al. 2010). Beyond soil type, climatic conditions further modulate the persistence of pH effects by controlling biochar degradation and aging dynamics, with faster biochar turnover in warm and humid regions requiring more frequent reapplication to maintain stable regulation (Yang et al. 2025b). Long-term or repeated biochar applications can sustain acid–base buffering benefits via progressive oxidation and organo-mineral complexation, which increases OCFGs abundance and proton adsorption capacity (Dong et al. 2017; Liu and Zhang 2012). In addition to these abiotic buffering mechanisms, rhizosphere microorganisms also exert important feedback effects on pH regulation. Biochar can provide favorable habitat for acid-producing taxa in alkaline soils, while driving microbial community shifts that stabilize

rhizosphere pH after initial liming in acidic soils, linking abiotic chemical buffering to biotic regulatory pathways (Dahlawi et al. 2018; Yang et al. 2025b).

Taken together, the acid–base buffering effects of biochar in the rhizosphere are governed by a clear hierarchy of controls. Pyrolysis temperature is the dominant first-order factor because it directly sets the initial pH and acid-neutralizing capacity of the biochar, with high-temperature biochar consistently producing stronger and more persistent liming effects than low-temperature biochar regardless of feedstock or soil type. Soil initial pH is the second-order control that determines the direction and magnitude of the biochar effect, with acidic soils showing large pH increases while neutral and calcareous soils show minimal change. Feedstock type and aging constitute third-order controls that modulate the magnitude and duration of pH effects within the ranges set by pyrolysis temperature and soil type. Microbial feedbacks act as a fourth-order control that can sustain or dampen pH changes over longer timescales. This hierarchy explains why biochar consistently raises pH in acidic soils but produces variable or negligible effects in neutral to alkaline soils, and why high-temperature biochar outperform low-temperature biochar for liming purposes across all soil types.

3.2 Sorption and desorption

Biochar mediates the fate of rhizosphere nutrients and contaminants via the synergistic effects of its hierarchical pore structure and surface chemical properties (Qiu et al. 2022). In the dynamic rhizosphere interface, fluctuations in pH, redox potential, and root exudate composition interact with biochar to govern the solid–liquid partitioning and mobility of target solutes (Sarma et al. 2024). Two fundamentally distinct retention mechanisms operate at the biochar surface. Adsorption refers to the binding of ions or molecules to the biochar surface via physical or chemical forces without forming a three-dimensional solid phase. Surface precipitation refers to the accumulation of sorbate on the biochar surface leading to the nucleation and growth of a new solid phase. While adsorption dominates at low sorbate concentrations, precipitation becomes increasingly important at higher loadings and elevated pH, and the two processes often coexist, making their experimental distinction challenging (Han et al. 2024; Singh et al. 2017). Regarding adsorption specifically, two primary binding modes govern metal and nutrient retention (Fig. 3). Ion exchange is a reversible electrostatic process where cations are attracted to negatively charged surface sites and can be replaced by other cations in solution. Surface complexation is the formation of stronger inner-sphere coordination bonds

between metal ions and specific OCFGs such as carboxyl and phenolic hydroxyl groups. Surface complexation generally exhibits higher binding affinity and greater resistance to leaching than ion exchange, but its capacity is limited by the density of reactive functional groups on the biochar surface (Uchimiya et al. 2011; Wei et al. 2025). Numerous studies have demonstrated that biochar's porosity and surface charge enable effective immobilization of toxic metals (e.g., lead, cadmium) and organic contaminants (e.g., polycyclic aromatic hydrocarbons, pesticides), reducing their migration toward plant roots (Das And Pandey 2025; Qiu et al. 2022). Its abundant OCFGs enhance sorption of polar organic compounds via electrostatic attraction, cation- π interactions, and surface complexation (Li et al. 2019), while low-molecular-weight organic acids (LMWOAs) in root exudates further modulate sorption by altering the protonation state of surface functional groups and localized rhizosphere geochemistry (Song et al. 2016).

Biochar aging significantly alters its sorption-desorption behavior through coupled physicochemical modifications that evolve over time scales ranging from months to decades. The key aging pathways and their consequences for sorption are as follows. (1) Surface oxidation progressively increases OCFG abundance, particularly carboxylic and phenolic groups, which enhances CEC and cation retention but may reduce sorption affinity for hydrophobic organic contaminants owing to increased surface hydrophilicity and water cluster formation (Wang et al. 2020). (2) Organo-mineral coating formation, driven by the interaction of dissolved organic matter, clay minerals, and metal oxides with biochar surfaces, partially occludes the intrinsic pore network and reduces accessible specific surface area, thereby decreasing sorption capacity for organic contaminants while simultaneously creating new reactive interfaces that enhance nutrient retention (Chen et al. 2022a, 2022b; Hagemann et al. 2017; Yang et al. 2018). (3) Physical fragmentation of biochar particles exposes fresh, unoxidized carbon surfaces with higher HC and sorption affinity, partially offsetting the decline in sorption capacity caused by surface oxidation and pore blockage (Wang et al. 2020). (4) Long-term field aging generally shifts the dominant metal immobilization mechanism from precipitation, driven by ash-derived carbonate and phosphate, toward surface complexation and ion exchange, driven by newly formed OCFGs. This shift has implications for long-term immobilization stability under changing environmental conditions such as soil acidification or increased salinity (Ren et al. 2022). These coupled aging effects mean that biochar sorption behavior evolves continuously, with some properties improving, such as CEC and cation retention,

while others decline, such as hydrophobic sorption capacity, and the net effect depends on the specific biochar-soil-solute combination (Wang et al. 2020).

These four aging pathways do not proceed uniformly across different soil microenvironments. The rhizosphere represents a distinct aging environment that can fundamentally alter both the trajectory and the rate of each pathway relative to bulk soil (Joseph et al. 2021). LMWOAs such as oxalic, citric, and malic acid, which reach exceptionally high concentrations in root exudates, accelerate surface oxidation by promoting the formation of reactive oxygen species at biochar surfaces and by directly donating protons to surface functional groups, thereby generating carboxylic and phenolic groups at rates exceeding those in bulk soil (Liu et al. 2017a). The abundant LMWOAs also modify pathway (2) by partially dissolving organo-mineral coatings and re-exposing internal pore surfaces, temporarily regenerating sorption sites that would otherwise remain occluded in the static bulk soil environment (Shabtai et al. 2024). Physical fragmentation via pathway (3) is intensified in the rhizosphere by root penetration forces and by the physical pressure exerted by arbuscular mycorrhizal hyphae exploring biochar pores, both of which mechanically disrupt biochar particles at rates exceeding those expected from abiotic wet-dry cycles alone (Hammer et al. 2014; Meng et al. 2024b). The dense microbial communities inhabiting biochar surfaces in the rhizosphere further accelerate the formation of secondary organo-mineral coatings through pathway (2), because microbial necromass and extracellular polymeric substances provide abundant organic precursors for coating formation (Weng et al. 2022). Frequent redox fluctuations driven by root oxygen release and microbial respiration promote dynamic iron (Fe) and manganese (Mn) oxide dissolution and re-precipitation cycles on biochar surfaces, which continually regenerate fresh mineral sorption phases while also periodically stripping protective coatings (Dong et al. 2023; Huang et al. 2023). Collectively, these rhizosphere-specific processes mean that biochar aging in the rhizosphere is both faster and more dynamic than in bulk soil, with the net effect depending on the interplay between accelerated oxidation, enhanced coating dissolution and re-formation, and intensified physical fragmentation.

Whereas the preceding discussion addresses how biochar sorption behavior evolves after soil incorporation, the intrinsic sorption properties of biochar are primarily determined during production. Pyrolysis conditions are the core determinant of biochar's intrinsic sorption properties. Low-temperature biochar (< 400 °C) retains higher OCFGs and volatile matter, exhibiting high ion exchange capacity and nutrient supply potential. In contrast, high-temperature biochar (> 600 °C) has a more condensed

aromatic structure, larger specific surface area, and higher sorption affinity for hydrophobic organic contaminants (Nkoh et al. 2021). Feedstock type also drives functional differences between biochar products. Wood-derived biochar generally has a larger specific surface area, crop residue-derived biochar typically has higher CEC, and manure-derived biochar is rich in macro- and micronutrients (Ippolito et al. 2020). From a mechanistic perspective, sorption processes encompass external surface adsorption and intraparticle diffusion into internal pore networks, with sorption site accessibility governed by pore size distribution and tortuosity (He et al. 2024b). Proton competition and hydration effects in strongly acidic soils ($\text{pH} < 5$) restrict intraparticle diffusion, reducing overall sorption efficiency (Wei et al. 2025), while mineral and organo-mineral coatings formed during aging can block pore entrances and slow diffusion kinetics (Gui et al. 2021; Yang et al. 2018). Conversely, root exudates can dissolve these coatings, re-exposing internal pore surfaces and increasing available sorption sites (Shabtai et al. 2024; Witzgall et al. 2024). Chemically, sorption is driven by surface functional group reactions and pH-mediated regulation of ionic speciation and surface charge density (Singh et al. 2017). In acidic soils, biochar amendment neutralizes acidity and provides abundant sorption sites for ionic contaminants and nutrients via electrostatic interactions and surface complexation (Liu et al. 2025; Teng et al. 2025), while also regulating phosphorus (P) speciation to mitigate leaching risk via modifying Fe redox cycling and aluminum (Al) oxide hydrolysis (Chen et al. 2022a, b). Biological mechanisms also modulate sorption–desorption processes at the biochar–soil interface. Biochar can adsorb microbial signaling molecules (e.g., N-acyl homoserine lactones) and disrupt quorum sensing in Gram-negative bacteria, altering functional gene expression and extracellular enzyme activity to modify contaminant bioavailability and biodegradation (Gorovtsov et al. 2020; Mukherjee et al. 2022). Furthermore, microbial colonization and biofilm formation on biochar surfaces provide additional sorption sites, while enhancing microbially mediated degradation of organic pollutants (An et al. 2022).

While the majority of sorption studies focus on heavy metals and organic contaminants, some studies have demonstrated that biochar can effectively immobilize radionuclides through the same ion exchange and surface complexation mechanisms described above. For instance, designer biochar activated with KOH achieved removal rates exceeding 80% for ^{137}Cs (cesium) and 47% for ^{90}Sr (strontium) even in the presence of competing cations, with spectroscopic evidence confirming that outer-sphere complexation between Cs and biochar surface functional groups was the dominant binding mode (Palansooriya

et al. 2022a, 2022b). In radioactively contaminated soils, biochar amendment significantly increased the distribution coefficient (K_d) of Cs isotopes from below 10 to over 100, demonstrating its capacity to reduce soil-to-plant transfer of cesium and strontium in contaminated environments (Hamilton et al. 2016). A recent comprehensive review further confirmed that biochar and its engineered derivatives exhibit remarkable efficiency in adsorbing and immobilizing a broad spectrum of radionuclides, thereby establishing biochar-based remediation as a viable and sustainable alternative to conventional approaches for managing nuclear-contaminated sites (Kordrostami And Ghasemi-Soloklui 2025).

The collective findings from sorption and desorption studies lead to three overarching conclusions. First, biochar sorption is not a static property but a dynamic function that evolves continuously with aging, transitioning from initial high-affinity hydrophobic sorption toward sustained hydrophilic nutrient retention over months to years. Second, the rhizosphere is not simply a recipient of biochar sorption services but an active modifier of sorption capacity. Root exudates simultaneously degrade sorption sites through acid-promoted dissolution and regenerate them through coating removal, creating a dynamic equilibrium that bulk soil studies cannot capture. Third, the net direction of biochar sorption effects depends on the dominant mechanism under the specific soil conditions. In acidic soils, the pH elevation and surface complexation dominate the functional outcome. In neutral to alkaline soils, ion exchange and physical adsorption govern nutrient and contaminant retention. These three principles provide a basis for predicting when biochar will function primarily as a contaminant immobilizer, a nutrient reservoir, or a dynamic exchange interface.

3.3 Complexation and precipitation

While sorption and desorption govern the partitioning of solutes between solid and solution phases, the long-term immobilization of metals and nutrients in the rhizosphere often involves stronger chemical bonds and the formation of discrete mineral phases. Accordingly, this section examines the two dominant mechanisms underlying such immobilization. Complexation and precipitation are two dominant geochemical mechanisms for immobilizing rhizosphere nutrients and contaminants, with performance governed by biochar surface functional groups and dynamic rhizosphere microenvironment chemistry (Li et al. 2019). Complexation refers to the formation of stable coordination bonds between metal ions and surface functional groups, either inner-sphere or electrostatic outer-sphere associations, without the formation of a discrete three-dimensional mineral phase.

Precipitation involves the formation of a new solid phase, such as metal phosphates, carbonates, or hydroxides, that nucleates either on the biochar surface or in the rhizosphere pore solution (Han et al. 2024; Uchimiya et al. 2011). For complexation reactions, as shown in Fig. 4, abundant OCFGs on biochar surfaces form stable inner-sphere coordination complexes with toxic metals, coupled with cation exchange processes via proton and base cation transfer (Uchimiya et al. 2011). Additional complexation pathways include cation- π interactions between divalent heavy metals and biochar's aromatic carbon matrix (Uchimiya et al. 2011). Targeted modification can significantly enhance the complexation capacity of biochar, as nitrogen-, phosphorus- and sulfur-modified biochars introduce high-affinity binding sites for heavy metals, while metal oxide-doped biochar (e.g., Mg-, Mn-, Fe-based composites) facilitates inner-sphere complexation via reactive hydroxyl groups and can also promote root iron/manganese plaque formation to provide additional rhizosphere complexation sites (Bostani et al. 2025; Chen et al. 2021b; Khan et al. 2023). Organic and microbial modifications further enrich the functional ligands of biochar. Chitosan-modified biochar reduces Cd accumulation in plant tissues, while microorganism-loaded biochar immobilizes metals via amino and carboxyl groups on microbial cell surfaces, with extracellular polymeric substances (EPS) further enhancing the stability of formed metal complexes (Gusiatin And Rouhani 2023; Qu et al. 2020). Dissolved organic matter released from biochar can also form soluble metal-organic complexes, reducing metal bioavailability under fluctuating salinity and water conditions (Su et al. 2025).

Multiple factors regulate complexation processes and their long-term stability. Prolonged soil aging reduces biochar's ash and reactive anion content while increasing OCFGs abundance and CEC, shifting the dominant Cd immobilization mechanism from precipitation to complexation and ion exchange (Ren et al. 2022). Rhizosphere pH acts as a core regulator of these processes. Alkaline biochar elevates rhizosphere pH to enhance deprotonation of negatively charged binding sites and strengthen complexation affinity, whereas acidic conditions promote protonation of surface functional groups and reduce overall metal binding capacity (Bostani et al. 2025). Root exudates can modulate complexation stability, promoting desorption of pre-complexed metals depending on biochar type and surface oxidation degree (Ren et al. 2022). Finer biochar particles also enhance complexation efficiency via larger specific surface area and higher exposure of reactive functional groups (Gui et al. 2021; Rehman et al. 2025).

For precipitation reactions, biochar drives the formation of sparingly soluble mineral precipitates via

supplying reactive anions and base cations, as well as regulating rhizosphere pH, with precipitation occurring both on biochar surfaces and in rhizosphere pore water (Han et al. 2024). In calcareous and alkaline soils, phosphate released from phosphorus-modified biochar reacts with Cd^{2+} and Pb^{2+} to form stable metal phosphate precipitates, a pathway enhanced under elevated pH (Bostani et al. 2025; Khan et al. 2023). Sulfate-reducing bacteria enriched in biochar-amended soils generate sulfide ions, promoting the formation of low-solubility metal sulfides (e.g., CdS) to further reduce metal bioavailability (Islam et al. 2024). Engineered biochar can be purposefully designed for targeted precipitation-based immobilization of contaminants. Hydroxyapatite-impregnated biochar supplies phosphate and elevates soil pH to stabilize cadmium phosphate precipitates, while zero-valent iron (ZVI)-modified biochar reduces highly toxic Cr(VI) to less mobile Cr(III) , which can precipitate as Cr(OH)_3 under neutral to alkaline soil conditions (Gusiatin And Rouhani 2023; Kumar And Radziemska 2022). Biochar also enhances biologically induced precipitation by providing a favorable habitat for ureolytic and sulfate-reducing bacteria, which generate carbonate and sulfide anions to drive metal mineral precipitation (Gusiatin And Rouhani 2023; Su et al. 2025). Precipitation processes are strongly regulated by soil physicochemical conditions. Acidic soils favor hydroxide and sulfate mineral precipitation via pH buffering effects, while water-saturated anaerobic conditions promote metal sulfide precipitation and co-precipitation with Fe/Mn oxides (Kumar And Radziemska 2022; Su et al. 2025). Conversely, long-term biochar aging depletes ash components and reactive anions, weakening precipitation capacity and shifting immobilized metals toward more labile fractions over time (Ren et al. 2022).

The juxtaposition of complexation and precipitation mechanisms reveals a critical functional transition in biochar-amended rhizospheres. A clearer conceptual overview is provided by summarizing the dominant immobilization mechanisms under varying environmental conditions in Table S2. Fresh biochar immobilizes metals predominantly through precipitation driven by ash-derived carbonate and phosphate. As biochar ages, this precipitation capacity declines while surface complexation capacity increases due to progressive OCFGs generation. This means that the dominant immobilization mechanism shifts from precipitation to complexation over time, with important practical implications. Under the precipitation-dominated early stage, metal immobilization is highly pH-dependent and vulnerable to acidification. Under the complexation-dominated later stage, immobilization becomes more resilient to pH fluctuations but more sensitive to competition from other

cations and to complexation with dissolved organic matter. This transition is essential for predicting long-term immobilization stability and for timing biochar reapplication in contaminated soils. From an operational perspective, the dominant mechanism can be predicted based on soil pH and redox status. In acidic soils, the precipitation of metal phosphates and hydroxides is often prevalent, especially when biochar supplies phosphate. In neutral to alkaline soils, surface complexation and cation exchange become increasingly important for metal retention. Under reducing conditions, such as in flooded soils, sulfide precipitation may dominate. These distinctions provide a practical guide for matching biochar type to soil conditions.

3.4 Redox mediation and electron transfer

Beyond the acid–base and sorption processes discussed above, biochar also participates directly in redox reactions that transform nutrients and contaminants. This section examines how biochar mediates electron transfer in the rhizosphere, a function that integrates its physical pore architecture with its surface chemistry. Biochar mediates rhizosphere redox processes and the transformation of nutrients and contaminants via its redox-active carbon matrix, persistent free radicals (PFRs), and reversible redox-active functional groups (Fig. 5), acting as an electron donor, electron acceptor, or electron shuttle to facilitate and accelerate microbial extracellular electron transfer (EET) in the rhizosphere (Joseph et al. 2015; Li et al. 2023). Two distinct electron transfer pathways operate in biochar-amended soils. Direct electron transfer occurs when biochar surface functional groups, such as quinone and hydroquinone moieties, donate or accept electrons directly to or from target contaminants in close contact with the biochar surface. This pathway is spatially constrained and depends on the accessibility of redox-active sites. In contrast, electron shuttling involves biochar reversibly accepting electrons from microbial metabolism and transferring them to distant electron acceptors, such as Fe(III) minerals. This extends the effective electron transfer distance beyond the immediate cell surface and overcomes the rate-limiting step of microbial EET (Xu et al. 2019, 2022; Yang et al. 2025c). A well-documented example of this redox regulation is the biochar-mediated reduction of highly toxic and mobile Cr(VI) to less toxic and sparingly soluble Cr(III). This transformation proceeds through both pathways. Phenolic and hydroxyl functional groups on the biochar surface directly reduce Cr(VI), while indirect electron shuttling enhances EET between metal-reducing microorganisms and Cr(VI). The latter pathway is widely recognized as the dominant mechanism in natural soil matrices (Xu et al. 2019, 2022). In addition to these

direct and shuttle-mediated electron transfers, biochar can facilitate the generation of reactive oxygen species (ROS), which participate in the oxidative transformation of organic contaminants and can influence plant stress responses, as detailed in the discussion of persistent free radicals below. For dissimilatory metal-reducing bacteria, EET across the cell envelope is often the rate-limiting step for reductive transformation of redox-sensitive substrates, and biochar overcomes this limitation by extending the effective electron transfer distance and accelerating bioreduction kinetics (Yang et al. 2025c). This electron transfer-mediated regulation is also applicable to other redox-sensitive metals and organic pollutants undergoing reductive degradation (Wang et al. 2024a). In flooded anoxic environments, biochar further participates in and modulates rhizosphere Fe and S redox cycling by mediating the reductive dissolution and oxidative precipitation of Fe-bearing minerals and associated S species, which directly govern the fate of rhizosphere nutrients and contaminants (Joseph et al. 2015).

In paddy rhizospheres, Fe plaque formed on rice root surfaces acts as a natural barrier to limit plant uptake of toxic metals such as Cd (Yuan et al. 2026). Biochar amendment promotes root Fe plaque formation, with significantly increased Cd sequestration within the plaque demonstrating its capacity to enhance metal immobilization at the root–soil interface (Xu et al. 2024b). Beyond direct electron transfer mediation, biochar modulates rhizosphere redox processes by altering soil physical structure and enhancing redox heterogeneity. Its hierarchical pore structure reduces soil bulk density and increases total porosity to enhance O₂ diffusion and support aerobic microbial metabolism and root respiration, while water retention in micropores creates localized anoxic micro-zones within predominantly oxic bulk soil (Leng et al. 2021). This dual effect expands the coexistence of aerobic-anaerobic interfaces in the rhizosphere, providing niches for microbial functional groups with distinct redox requirements and enabling the simultaneous occurrence of redox reactions that are thermodynamically incompatible in homogeneous environments (Hussain et al. 2017; Xiao et al. 2018). These aerobic-anaerobic interfaces further intensify the coupled cycling of Fe, Mn, and S in the rhizosphere. In anoxic micro-zones, Fe- and Mn-reducing bacteria mediate the reductive dissolution of insoluble Fe(III)/Mn(IV) oxides into bioavailable Fe(II)/Mn(II), a process facilitated by biochar as an electron shuttle. These reduced metal species diffuse to adjacent oxic micro-zones, where they are re-oxidized and precipitate as secondary Fe/Mn oxides on soil particles and root surfaces (Ameloot et al. 2013; Dong et al. 2023; Li et al. 2024a; Yang et al. 2025c). This cyclic process

directly regulates the fate of associated nutrients (e.g., P) and contaminants (e.g., As, Cd) via coupled sorption and co-precipitation (Wang et al. 2022a). In strongly anoxic micro-zones, biochar also facilitates sulfate-reducing bacteria to generate sulfide, driving toxic metal sulfide precipitation and forming Fe-S phases that modulate rhizosphere P fixation and release (Fu et al. 2024).

Biochar's PFRs represent an emerging frontier in understanding its redox behavior (Alfei And Pandoli 2024; Chen et al. 2025a). PFRs are stabilized unpaired electrons within the condensed aromatic carbon matrix. They are formed during biomass pyrolysis through the thermal decomposition of lignin, cellulose, and other organic precursors. Their concentration, type, and stability are strongly governed by pyrolysis temperature and feed-stock composition (Chen et al. 2024a; Wang et al. 2022b). PFRs participate in redox reactions through multiple pathways, directly donating electrons to reducible contaminants such as Cr(VI) and nitroaromatic compounds, or generating ROS including hydroxyl radicals ($\cdot\text{OH}$), superoxide anion radicals ($\text{O}_2^{\cdot-}$), and hydrogen peroxide (H_2O_2) upon contact with oxygen and water (Fang et al. 2014a; Yu et al. 2023). These ROS can oxidatively degrade organic pollutants or, conversely, induce oxidative stress in rhizosphere microorganisms and plant roots, representing a potential negative effect that requires careful evaluation (Liao et al. 2014; Zhang et al. 2024a). PFRs also influence soil microbial community composition (Gorovtsov et al. 2020; Yang et al. 2023). Studies have shown that biochar-associated free radicals can reduce soil bacterial diversity and alter coenzymatic stoichiometry, with oxygen-centered PFRs generally exhibiting higher reactivity and greater biological effects than carbon-centered PFRs (Yang et al. 2023). As discussed in Sect. 3.2, biochar aging leads to a progressive decline in PFR concentration and reactivity. Consequently, PFR-mediated effects are most pronounced in the first months to years after application. Over longer timescales, redox regulation transitions toward mechanisms involving surface functional groups and electron shuttling (Chen et al. 2024b; Joseph et al. 2015; Wang et al. 2020). Surface alcoholic hydroxyl groups can be oxidized to carbonyl groups during PFR-mediated reactions, quenching free radicals and altering the overall redox behavior of amended soils (Li et al. 2023). Biochar can also buffer excessive increases in soil redox potential, promote the activity of Fe- and sulfate-reducing bacteria, and inhibit the oxidative dissolution of CdS precipitates (Li et al. 2023). The redox activity of biochar is intrinsically governed by pyrolysis conditions, with the abundance of reductive surface functional groups generally decreasing with increasing pyrolysis temperature, and evolves dynamically during

field aging via organo-mineral coating formation, particle fragmentation, and exposure of fresh redox-active surfaces (Joseph et al. 2010).

The redox mediation functions of biochar integrate the physical and chemical pathways discussed throughout this section. Biochar's capacity to create aerobic-anaerobic interfaces through its pore structure couples directly with its electron shuttling capacity to sustain Fe, Mn, and S redox cycling. The simultaneous occurrence of oxidative and reductive micro-zones in biochar-amended rhizospheres means that biochar does not simply shift the bulk redox potential in one direction. Instead, it expands the redox heterogeneity of the rhizosphere, enabling coupled transformations that would otherwise be spatially or temporally separated. This principle explains why biochar can simultaneously promote Fe plaque formation on roots through Fe(II) oxidation while facilitating Fe(III) reduction and Cd release in adjacent anoxic microsites. The net ecological outcome, whether contaminant immobilization or nutrient mobilization, depends on the spatial balance between these micro-zones, which is in turn governed by soil water status, root oxygen release, and biochar pore architecture.

4 Microbial ecology and functional responses in the biochar rhizosphere

4.1 Creation of microbial habitats

Biochar provides a favorable and protective microbial habitat in soil via its hierarchical physical structure and tailored surface chemistry, which form sheltered microsites and reactive interfacial regions for microbial colonization (Głuszek et al. 2017; Weng et al. 2022). Its high porosity and large specific surface area cover interconnected macropores (>50 nm), mesopores (2–50 nm), and micropores (<2 nm) (per IUPAC definition), offering sufficient colonization space and physical refuge for soil microorganisms (Lehmann et al. 2015; Zhao et al. 2013b). As shown in Fig. 6, biochar pores can harbor bacterial colonies and fungal hyphae, reducing their exposure to predators such as protozoa and nematodes via physical shelter and spatial separation (Jaafar et al. 2014; Warnock et al. 2007). This physical protection represents a direct habitat effect, distinct from indirect nutrient- or pH-mediated mechanisms that also shape microbial communities in biochar-amended soils. Specifically, biochar influences rhizosphere microbial ecology through four complementary but mechanistically distinct pathways, as summarized in Table 2. The first is the direct habitat effect, where biochar pores and surfaces provide physical niches for colonization and refuge from predators. The second is nutrient-mediated effects, where biochar supplies labile carbon and retains nutrients such as ammonium and phosphate, thereby alleviating microbial

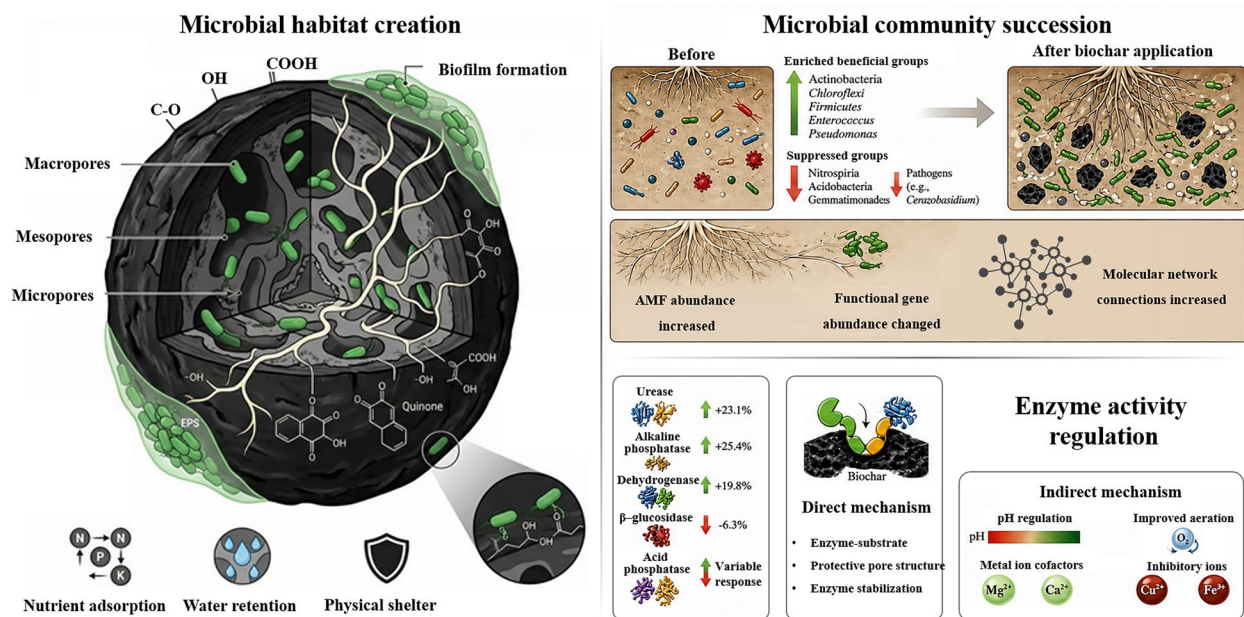


Fig. 6 Mechanisms underlying biochar-mediated regulation of rhizosphere microorganisms and enzyme activities

nutrient limitation and stimulating growth. The third is pH-mediated effects, where biochar-driven shifts in rhizosphere pH alter the solubility of nutrients and toxins, restructuring microbial community composition toward taxa adapted to the modified pH regime. The fourth is direct signaling effects, where biochar adsorbs or releases signaling molecules including quorum sensing signals and root exudate components, thereby modulating microbial communication and gene expression independently of nutrient or pH changes (Bolan et al. 2023; Gorovtsov et al. 2020; Masiello et al. 2013; Mukherjee et al. 2022). Beyond these four pathways, biochar also shapes a distinct chemical microenvironment via its strong capacity to adsorb organic compounds, essential nutrients, and water, shifting rhizosphere microbial community structure toward taxa that benefit from enhanced resource retention and stability (Arshad et al. 2024; Sun et al. 2016). Numerous studies have documented selective enrichment of beneficial functional groups, including phosphate-solubilizing microorganisms, in biochar-amended soils, with labile carbon fractions in biochar stimulating microbial activity and its interconnected pore network facilitating continuous biomass accumulation (Chang et al. 2025; Zhao et al. 2020).

Beyond pore structure, biochar surface chemistry directly regulates microbial colonization and metabolic activity (Zhang et al. 2022). OCFGs such as carboxyl, hydroxyl, and quinone moieties confer a net negative charge on biochar surfaces, adsorbing nutrients and contaminants while providing stable binding sites for

microbial cell attachment (Bolan et al. 2023; Wang et al. 2025). After initial attachment, microorganisms often form structured biofilms embedded in EPS, which stabilize cell adhesion and provide additional reactive sites for pollutant immobilization (Prabhakaran et al. 2016). These habitat-related effects of biochar involve distinct ecological trade-offs. Biochar can reduce plant dependence on arbuscular mycorrhizal fungi (AMF) symbioses when it increases soil nutrient availability, and some biochar products can inhibit sensitive microbial groups if they contain elevated levels of heavy metals, PAHs, or other toxic compounds (Gryndler et al. 2006; Warnock et al. 2010). Microbial colonization on biochar is spatially heterogeneous, as internal pores and external surfaces differ greatly in nutrient accessibility and localized toxicity. This colonization process also shows strong time dependence. Fresh biochar is often less favorable for microbial colonization due to inherent phytotoxicity or limited accessible nutrients, while aging over months to years reduces toxic compound levels and optimizes biochar surface properties to increase colonization intensity (Quilliam et al. 2013a, 2013b).

Biochar inherent heterogeneity is a major driver of variable habitat quality. Feedstock type and pyrolysis conditions jointly control pore development and surface chemical properties, with higher pyrolysis temperatures often increasing total porosity and specific surface area to expand colonization space (Dai et al. 2021; Jaafar et al. 2015). However, habitat quality depends not only on total porosity, but also on pore size distribution and

Table 2 Mechanisms by which biochar shapes the rhizosphere microbiome and associated ecological tradeoffs

Mechanism category	Key process	Positive outcome	Ecological trade-off/risk	Reference
Direct habitat effects	Pore colonization, physical refuge from predators	Increased microbial biomass, biofilm formation, protection of hyphae/bacteria	Pore blockage by mineral-organic coatings; reduced AMF dependence; localized heterogeneity	(Jaafar et al. 2014; Lehmann et al. 2011; Quilliam et al. 2013a)
Nutrient-mediated effects	Labile C supply, NH_4^+ / PO_4^{3-} retention	Alleviation of nutrient limitation, stimulation of copiotrophs and P-solubilizers	Carbon pulse may favor opportunistic pathogens; nutrient-rich conditions can weaken AMF symbiosis	(Bolan et al. 2023; Chang et al. 2025; Gryndler et al. 2006)
pH-mediated effects	Liming, shifts in Al^{3+} / Mn^{2+} toxicity	Restructuring of acid-sensitive taxa, enhanced nutrient bioavailability	Alkaline stress on acid-adapted communities; transient pH spike	(Gorovtsov et al. 2020; Mukherjee et al. 2022)
Direct signaling effects	Adsorption/release of quorum sensing signals, root exudate modulation	Altered microbial communication, expression of beneficial traits	Potential disruption of native signaling networks; effects poorly characterized	(Masiello et al. 2013; Bolan et al. 2023)

connectivity, which control water and gas transport and microbial access to nutrients within the pore network (Hardie et al. 2014; Schnee et al. 2016). After soil incorporation, mineral and organic coatings gradually accumulate on biochar surfaces and block pore entrances, reducing accessible habitat space and altering long-term colonization patterns (Hagemann et al. 2017). At the bulk soil scale, biochar's habitat effects are concentrated in localized biochar-associated microsites, with impacts diluting significantly with soil depth (Quilliam et al. 2013a). Overall, the effectiveness of biochar as a microbial habitat depends on interacting controls from biochar inherent properties, soil environmental conditions, and long-term aging dynamics (Lehmann et al. 2011; Pingree et al. 2022).

While the above discussion identifies the potential for negative microbial effects, the prevalence of such effects and the specific biochar types associated with them warrant systematic evaluation. A comprehensive review concluded that biochar application does not typically exert toxic effects on soil organisms and often stimulates microbial activity, with the outcome strictly determined by feedstock type and pyrolysis temperature (Godlewska et al. 2021). Negative effects are concentrated in specific biochar categories (Table 3). Feedstock is the dominant control. Sewage sludge biochar consistently carries elevated heavy metal loads, with Cd posing a considerable ecological risk relative to other feedstocks (Zhou 2015). Manure-derived biochar, particularly from cattle and poultry litter, can cause strong microbial inhibition primarily due to salinity stress from high potassium concentrations rather than heavy metal toxicity (Cantou et al. 2025). In contrast, wood-derived biochar produced at moderate to high temperatures rarely exhibits toxicity (Godlewska et al. 2021; Cantou et al. 2025). Pyrolysis temperature exerts a secondary control. Biochar produced at low temperatures (350–400 °C) is more frequently toxic than those produced above 500 °C, because

they retain volatile organic compounds and soluble salts that inhibit microbial activity (Cantou et al. 2025). PAH concentrations peak in the 400–500 °C range and decline above 600 °C (Keiluweit et al. 2012), and environmentally persistent free radicals formed at higher temperatures can induce oxidative stress in microbial cells (Godlewska et al. 2021). Application rate introduces a third-order control. Negative effects are most commonly reported at amendment levels exceeding 50 t ha⁻¹, whereas rates below 30 t ha⁻¹ rarely produce measurable microbial inhibition (Brtnicky et al. 2021; Nissen et al. 2021). Importantly, the contaminants responsible for short-term toxicity, particularly volatile organic compounds, are not persistent in soil and diminish within weeks to months (Nissen et al. 2021). Biochar derived from sewage sludge, poultry litter, or cattle manure warrants mandatory ecotoxicological screening before field application, particularly when produced at temperatures below 500 °C. Wood- and crop residue-derived biochar produced above 500 °C at application rates below 30 t ha⁻¹ pose minimal risk to soil microbial communities and can be considered suitable for agricultural use without extensive pre-testing. Taken together, the net effect of biochar on the rhizosphere microbiome reflects a balance between habitat-mediated benefits and toxicity-mediated risks, with feedstock type, pyrolysis temperature, and application rate serving as the primary levers for shifting this balance toward a desired outcome.

4.2 Microbial community assembly, diversity, and network structure

Biochar mediates rhizosphere microbial succession across multiple dimensions, including community composition and alpha diversity, shifts in core and indicator taxa, and changes in microbial interaction network complexity and stability (Jaafar et al. 2015). These responses vary significantly with crop species, biochar properties, site edaphic conditions, and time since application, with

Table 3 Risk factors for negative microbial effects of biochar and recommended screening criteria

Risk factor	High-risk characteristics	Low-risk characteristics	Evidence/recommendation
Feedstock	Sewage sludge (Cd, heavy metals), manure (high K salinity)	Wood, crop residue	Mandatory ecotoxicological screening for sludge/manure biochars (Zhou 2015; Cantou et al. 2025)
Pyrolysis temperature	350–500 °C (VOCs, soluble salts, peak PAHs)	> 500 °C (reduced VOCs, lower PAHs, but note persistent free radicals)	Low-temperature biochars more frequently toxic (Godlewska et al. 2021; Keiluweit et al. 2012)
Application rate	> 50 t ha ⁻¹	< 30 t ha ⁻¹	Negative effects rare below 30 t ha ⁻¹ (Brtnicky et al. 2021; Nissen et al. 2021)
Post-application aging	Fresh biochar (residual phytotoxins)	Aged months–years (toxins diminished)	Short-term toxicity is often transient; aging reduces VOCs (Nissen et al. 2021; Quilliam et al. 2013b)

residual effects persisting for multiple years after a single application (Gorovtsov et al. 2020; Wang et al. 2025). A global meta-analysis reported that biochar amendment generally increases AMF abundance, microbial biomass carbon, and functional richness across terrestrial ecosystems, while actinobacteria abundance and basal soil respiration tend to decline, with patterns consistent across study designs and experimental durations (Xu et al. 2020). Long-term field trials illustrate that these microbial responses can be stable and dose-dependent. In a continuous soybean monocropping system, ten years of continuous biochar application enriched beneficial bacterial and fungal taxa while suppressing soil-borne pathogens, with higher application rates producing more pronounced shifts in microbial community structure (Wu et al. 2025a, 2025b).

In addition to altering community composition, biochar also reshapes the interactions among taxa. Several studies have reported that biochar amendment increases network complexity, reflected in higher node counts, edge density, and average clustering coefficients, while simultaneously reducing network modularity. These structural changes suggest that biochar promotes more interconnected microbial communities with greater functional redundancy. However, increased network complexity is not universally observed. Under certain conditions, such as high biochar application rates or specific soil types, biochar can reduce network connectivity or increase modularity, indicating that network responses are context-dependent. Keystone taxa, defined as highly connected nodes that exert disproportionate influence on community structure and function, also shift markedly after biochar addition. Biochar tends to enrich keystone taxa affiliated with Actinobacteriota, Proteobacteria, and Chloroflexi, many of which possess metabolic capabilities related to cellulose degradation, phosphate solubilization, or denitrification. The enrichment of these keystone groups suggests that biochar not only alters overall community composition but also restructures the functional backbone of the microbial network, potentially enhancing the resilience and stability of rhizosphere microbiomes under environmental stress (Cui et al. 2024; Dai et al. 2021; Zhou et al. 2024). It is important to note, however, that increased microbial diversity or network complexity does not inherently confer beneficial outcomes. In some scenarios, elevated diversity reflects the proliferation of opportunistic or pathogenic taxa responding to biochar-derived carbon pulses, and shifts in community composition rather than diversity per se may be the more ecologically meaningful indicator of soil health (Xu et al. 2020; Yang et al. 2023). These context-dependent network responses can be reconciled by recognizing that biochar increases connectivity when it alleviates resource

limitations, such as in nutrient-poor or acidic soils, but may decrease connectivity when it introduces toxic compounds or when nutrients are already abundant, thus shifting the competitive balance among taxa.

Biochar effects on rhizosphere microbial communities are often taxon-specific, primarily driven by biochar-induced changes in rhizosphere pH and nutrient availability (Deinert et al. 2024). In acidic low-organic-carbon soils, biochar often increases the abundance of functional decomposer groups such as Actinobacteriota and Chloroflexi that contribute to cellulose and lignocellulose turnover. In eucalyptus seedling plantations, co-application of biochar with plant growth-promoting rhizobacterium (PGPR) *Bacillus megaterium* outperformed single inputs, increasing soil nutrient availability and enriching beneficial taxa including Actinobacteria, Gemmatimonadota and Cyanobacteria (Ren et al. 2020). In arsenic-contaminated paddy soil, modified biochar altered the abundance of *Geobacter* and *Nitrososphaera*, linking effects on arsenic immobilization to soil nitrogen transformation (Liu et al. 2017b). In saline-alkaline ecosystems, biochar combined with bio-organic fertilizer enriched beneficial taxa including Actinobacteria and *Micromonospora*, with soil nitrogen and phosphorus availability exerting a stronger influence on bacterial community structure than salinity (Gu et al. 2022). Residual effects of biochar on soil microbial communities can persist long after application ceases. Sewage sludge-derived biochar altered maize rhizosphere microbial communities five years after application stopped, with biochar produced at 500 °C increasing bacterial diversity and enriching functional groups linked to organic matter decomposition and nutrient cycling (Cruz et al. 2024).

4.3 Functional gene and metabolic responses

Biochar amendment reshapes the abundance of functional genes governing nitrogen and phosphorus cycling in the rhizosphere. A meta-analysis of field studies found that biochar increased the abundance of ammonia-oxidizing archaea *amoA*, *nirK*, *nirS*, and *nosZ* genes by 25.3%, 32.0%, 14.6%, and 17.0%, respectively (Xiao et al. 2019). In apple orchard soils, biochar enhanced nitrogen-fixing genes and N₂O reduction genes in the rhizosphere, reducing N₂O concentrations by 13.7% to 35.1% (Cao et al. 2021). Similarly, for phosphorus, biochar elevated the copy numbers of *phoC* and *phoD* genes encoding acid and alkaline phosphatases, supporting organic phosphorus mineralization and plant phosphorus uptake (Deinert et al. 2024). Biochar can interact synergistically with AMF to upregulate phosphorus cycling functional genes, with stronger effects under low phosphorus conditions (Meng et al. 2024b). Beyond nutrient cycling genes, biochar simultaneously modulates carbon degradation and

carbon fixation genes. A ^{13}C study of maize rhizosphere showed that biochar enhanced both sets of genes within a single growing season, with bacterial functional traits predominantly controlling the rhizosphere priming effect (He et al. 2024a). Biochar also shapes the structure of autotrophic microbial communities harboring *cbbL* and *cbbM* genes, which encode the key enzyme in the Calvin cycle, coupling CO_2 fixation with iron oxidation and nitrogen reduction pathways in the rhizosphere (Jiang et al. 2025).

At the metabolic level, microbial carbon use efficiency (CUE), the proportion of carbon assimilated into biomass relative to total uptake, determines whether the microbiome acts as a net carbon source or sink. Biochar has been proposed to increase microbial CUE by shifting the physical and chemical soil environment to a more favorable state, which can reduce the metabolic maintenance costs of microbes and alleviate nutrient limitation through improved nutrient retention (Giagnoni and Renella 2022). Experimental evidence supports this concept, showing that a biochar application of 30 Mg ha^{-1} increased microbial CUE and induced a negative priming effect, thereby reducing the mineralization of both native soil organic carbon and freshly added labile carbon (Kalu et al. 2024). Closely linked to CUE is the rhizosphere priming effect, where biochar-derived labile carbon stimulates or suppresses native SOC decomposition. Biochar can induce positive priming by providing energy for decomposers, or negative priming through sorption of organic matter onto biochar surfaces and enhanced microaggregate protection (Wang et al. 2016; Weng et al. 2017). The balance between these opposing effects is dynamic and context-dependent. The interplay between microbial growth, CUE, and turnover ultimately governs microbial necromass accumulation, a major precursor of stable soil organic matter. An eleven-year field trial showed that biochar increased microbial necromass carbon by 13.9%, with bacterial necromass more readily enriched than fungal necromass (Chen et al. 2024c). However, the direction of this effect depends on soil context. A four-year field experiment reported that biochar reduced microbial necromass carbon by 7.5% to 10.5%, attributed to a shift toward K-strategists and intensified microbial nitrogen limitation (Ma et al. 2025). A nine-year Mollisol study comparing straw and biochar found divergent pathways: straw enhanced SOC primarily through microbial necromass entombment, whereas biochar enhanced SOC primarily through biochemical protection of its recalcitrant aromatic carbon (Yuan et al. 2025b).

Biochar also influences broader ecological functions of the rhizosphere microbiome. Biochar has been reported to reduce the transmission of antibiotic resistance genes

from bulk soil and rhizosphere to plant endophytes by 1.2–2.2 orders of magnitude, linked to suppression of mobile genetic elements and shifts in bacterial host community structure (Zhou et al. 2024). Under stress contexts, biochar can stabilize rhizosphere bacterial communities during aboveground pathogen infection, and improve plant drought and salinity tolerance by enriching stress-resilient microbial functional groups and altering root exudate profiles (Fahad et al. 2023; Wu et al. 2025b). In paddy field systems, biochar effects on methane and nitrous oxide emissions depend strongly on pyrolysis temperature and application rate, with rhizosphere functional indicators showing stronger explanatory power for nitrous oxide emission variation than bulk soil indicators (Qi et al. 2023).

4.4 Regulation of rhizosphere enzyme activity

Biochar amendment alters the activity of a wide range of rhizosphere extracellular enzymes (Fig. 6), including urease, phosphatases, sucrase and catalase, with response direction and magnitude differing significantly among enzyme classes and soil types (Zhang et al. 2019). Global meta-analyses indicate that biochar exerts bidirectional effects on soil extracellular enzyme activity. One comprehensive synthesis reported an average 6.3% reduction in hydrolytic enzyme activity, including α -glucosidase, β -cellobiosidase, and β -glucosidase, with inhibitory effects increasing in line with higher biochar application rates and pyrolysis temperatures (Yin et al. 2021; Zhang et al. 2019). In contrast, dehydrogenase activity is consistently stimulated by biochar amendment, with meta-analyses reporting an average 19.8% increase across published studies (Pokharel et al. 2020). For key nutrient cycling enzymes, the effects of biochar are predominantly positive. Meta-analyses indicate that biochar increases urease and alkaline phosphatase activities by an average of 23.1% and 25.4%, respectively, with significant increases also reported for nitrite reductase and N-acetylglucosaminidase across multiple soil types (Pokharel et al. 2020). However, these positive responses are not universal, and rate thresholds and diminishing returns have been widely reported across studies. Low biochar application rates often stimulate enzyme activity, while excessive application rates may cause inhibition or deliver no additional functional benefit (Huang et al. 2017). Soil type is a dominant factor regulating enzyme responses to biochar amendment (Rani And Garg 2025). Stronger stimulation of microbial biomass carbon, alkaline phosphatase, dehydrogenase, and urease activity is often observed in fine-textured soils (clay, clay loam) and acidic soils ($\text{pH} < 6.5$) (Pokharel et al. 2020). Land use context further shapes these responses. Upland

agricultural soils show average urease increases of 32.6–66.4%, paddy soils show 2.13–2.90-fold increases relative to controls, while greenhouse facility soils show highly variable outcomes (Rani And Garg 2025; Zhao et al. 2023). Pyrolysis temperature is another key determinant of enzyme responses. Low-temperature biochar produced below 500 °C contains higher levels of labile carbon and more consistently promotes the activity of multiple extracellular enzymes, while high-temperature biochar produced at or above 500 °C may contain higher levels of PFRs and impose oxidative stress on soil microbial communities, which can inhibit enzyme activity in some soil types (Gregory et al. 2014; Jin et al. 2024; Liao et al. 2022; Lehmann et al. 2011; Zhang et al. 2023).

The enzyme responses described above arise from a combination of direct and indirect mechanisms. Direct effects arise primarily from biochar's high specific surface area and strong adsorption capacity. Biochar can adsorb both enzymes and their corresponding substrates, which protects enzymes from proteolytic degradation and provides localized reaction platforms. Conversely, excessively strong adsorption can also reduce enzyme activity by limiting substrate access to enzyme active sites (Demisie et al. 2014; Prayogo et al. 2014). Indirect effects occur when biochar shifts key soil physicochemical properties and microbial community structure, including pH, aeration, and water retention capacity (Fahad et al. 2023; Liao et al. 2022). The alkalinity of most biochar products can neutralize acidic soils and optimize conditions for pH-sensitive enzymes; its pore networks provide protected microbial habitat, stimulating microbial growth and increasing the synthesis and secretion of extracellular enzymes. Ions released from biochar can also modulate enzyme activity, acting as cofactors in some contexts or inhibiting activity when toxic metals are present. Temporal dynamics also play a critical role in shaping enzyme responses to biochar amendment. In the short term, biochar can rapidly increase dehydrogenase and phosphatase activities, especially when co-applied with organic manure. Over longer timescales, biochar can integrate with the soil matrix, support the accumulation of stable soil organic matter, and maintain higher enzyme activity via sustained carbon substrate supply and long-term pH stabilization (Lopes et al. 2021; Idbella et al. 2024; Parasar and Agarwala 2025). Biochar aging also modifies enzyme responses over time. Depletion of labile carbon fractions may reduce the activity of some enzymes, while abiotic aging can increase laccase and peroxidase activity via changes in the aromatic and aliphatic group content of biochar surfaces (Pokharel et al. 2020; Yang et al. 2023).

5 Biochar mediated biogeochemical cycling of key rhizosphere elements

The rhizosphere, as the core hotspot of plant–soil biochemical and physical interactions, is a central hub for terrestrial biogeochemical cycling, governing the migration and transformation of key elements in the atmosphere–plant–soil continuum. Biochar regulates rhizosphere elemental cycling through coupled physicochemical modification, microbial community reshaping, and root physiological regulation, with core regulatory pathways and outcomes summarized in Fig. 7.

5.1 Carbon cycle

With its stable aromatic carbon framework and high porosity, biochar is widely recognized as a critical amendment for regulating rhizosphere carbon cycling and enhancing soil carbon sequestration (Gui et al. 2025; Lehmann et al. 2021; Stewart et al. 2013), with effects driven by the coupled regulation of carbon inputs, transformation pathways and stabilization processes (Chen et al. 2024c). Carbon input is the starting point of rhizosphere carbon cycling, and biochar increases carbon inputs through direct and indirect pathways (Luo et al. 2017). Directly, the recalcitrant aromatic carbon in biochar contributes to the stable soil organic carbon pool with centennial to millennial residence times, acting as a persistent supplement to long-term soil carbon stocks (Wang And Kuzyakov 2024; Woolf et al. 2021). Indirectly, biochar promotes root growth by optimizing soil physical structure and nutrient-water availability, driving greater rhizodeposition inputs. Rhizodeposits, which account for 10% to 50% of photosynthetically fixed carbon, have 2–13 times higher stabilization efficiency than litter-derived carbon, as they are rapidly assimilated by microorganisms and converted into stable microbial necromass carbon (Oguntunde et al. 2008; Pausch And Kuzyakov 2018; Sokol et al. 2019; Wang And Kuzyakov 2024). Correspondingly, biochar can increase the belowground recovery of newly fixed root-derived carbon by 20%, and can further regulate rhizodeposit bioavailability via adsorption to reduce rapid mineralization and carbon losses (Weng et al. 2017).

Shifts in rhizosphere priming effects are the central mechanism by which biochar mediates rhizosphere carbon transformation (Li et al. 2021a; Luo et al. 2023). Shortly after application, labile fractions in biochar stimulate r-strategist microorganisms, triggering a short-term positive priming effect that accelerates native soil organic carbon mineralization, with more pronounced effects for low-temperature biochar (He et al. 2024a; Sarfraz et al. 2019; Woolf and Lehmann 2012). With progressive aging, labile fractions are depleted, and the combined

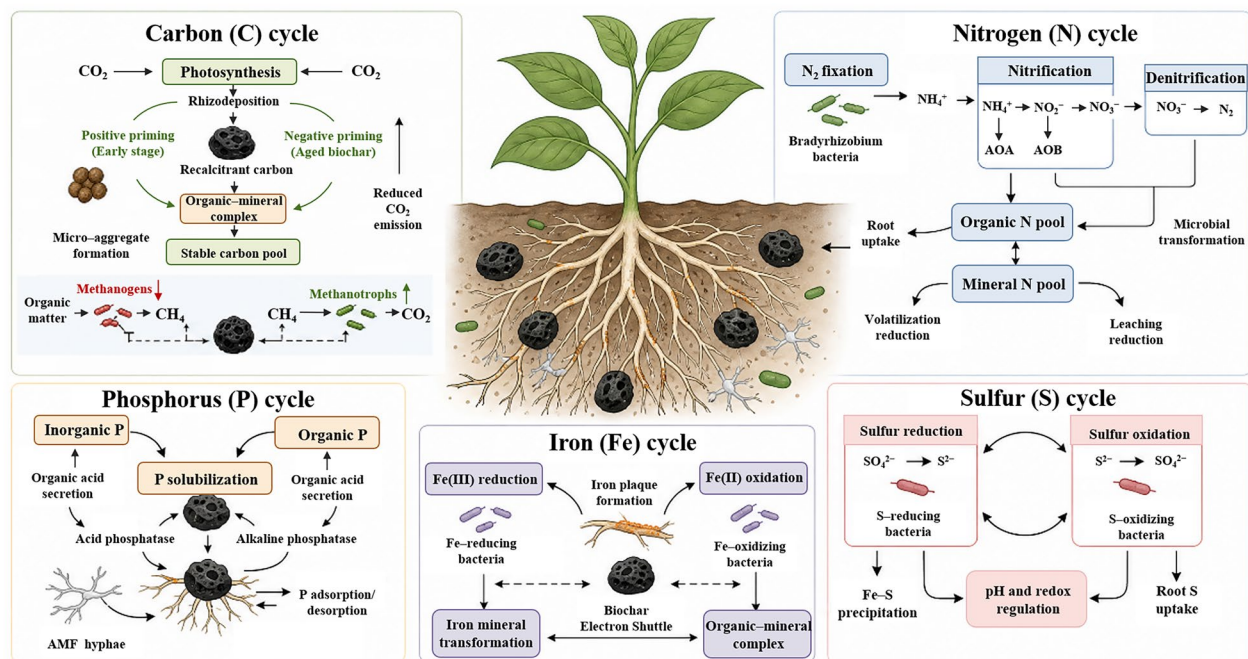


Fig. 7 Mechanisms underlying biochar-mediated regulation of rhizosphere key elemental cycles

effects of microbial pore refuge, organic carbon sorption, and microbial community shifts reduce organic carbon mineralization, driving a transition from positive to negative priming effects. Meta-analyses have reported over 5.5% reduction in soil organic carbon mineralization under long-term biochar amendment, which aligns with the increased dominance of K-strategist taxa and higher microbial carbon use efficiency (Chen et al. 2024c; He et al. 2024a; Wang et al. 2020). Biochar also alters the abundance of carbon degradation and fixation functional genes (e.g., *cbhI*, *cbhL*), providing an additional regulatory pathway for rhizosphere carbon transformation (Parasar And Agarwala 2025; Weng et al. 2022).

These carbon transformation processes ultimately drive enhanced carbon stabilization, a key outcome of biochar-rhizosphere interactions. Synchrotron-based analyses show that biochar accelerates the formation of <250 μm micro-aggregates, which provide physical protection for soil organic carbon, and increases the retention of root-derived carbon in the <53 μm stable organo-mineral fraction by 6% (Weng et al. 2017). Biochar also enhances plant photosynthetic carbon fixation by improving soil moisture and nutrient availability, protects chloroplast structure, and enhances Calvin cycle enzyme activity and alleviate oxidative stress in contaminated soils, supporting greater plant carbon capture (Lei et al. 2024). In terms of greenhouse gas outcomes, biochar generally reduces CO_2 emissions via carbon stabilization, though responses vary with soil type. Beyond CO_2 , biochar also

modulates methane (CH_4) emissions from the rhizosphere, particularly in paddy systems where methanogenic and methanotrophic processes are active (Lee et al. 2023). Biochar can suppress CH_4 emissions by increasing soil porosity and aeration, which enhances the activity and abundance of methanotrophic bacteria, and by shifting the balance between methanogens and methanotrophs. A four-year field study in a double rice cropping system demonstrated that biochar amendment at 24 and 48 t ha^{-1} reduced annual CH_4 emissions by 20–51%, with the abundance ratio of methanogens to methanotrophs decreasing by 11–31% each year, and this ratio positively correlated with CH_4 emissions (Wang et al. 2019d). This microbial community restructuring was accompanied by an increased relative abundance of basophilic methanotrophs such as *Methylobacterium* and a decline in *Methylocaldum*, while methanogen communities shifted toward enrichment of *Methanocella* and *Methanospirillum* and reductions in *Methanoregula* and *Methanosaeta*. A regional meta-analysis of East Asian rice paddies further confirmed that biochar significantly reduced CH_4 emissions, with the magnitude of suppression depending on feedstock type, pyrolysis temperature, and application rate (Lee et al. 2023).

The stability of biochar-mediated carbon sequestration is challenged by global warming, which accelerates soil organic matter decomposition. Biochar amendment can lower the temperature sensitivity (Q_{10}) of soil organic carbon decomposition by increasing microbial carbon

Table 4 Buffering effects of biochar on rhizosphere carbon and nitrogen cycling under climatic stresses

Climatic stress	Element cycle	Buffering mechanism	Key outcome	Reference
Global warming (temperature increase)	C	Increases microbial CUE by 11–39%; shifts community toward K-strategists (fungi, Actinobacteria)	Reduces temperature sensitivity (Q_{10}) of SOC decomposition; aged biochar shows stronger effect	(Chen et al. 2025b; Fang et al. 2014b)
	N	High application rates suppress warming-induced stimulation of N_2O emissions	Suppresses warming-driven N_2O emission increases in tropical soils	(Rittl et al. 2021)
Drying–rewetting cycles	C	Porous structure protects microbes from rewetting stress; adsorbs root-derived carbon; promotes aggregate formation; retains soil moisture	Reduces CO_2 pulses upon rewetting and stabilizes decomposition rates	(Rhymes et al. 2026; Weng et al. 2022; Pan et al. 2026)
	N	Adsorbs ammonium; reduces nitrate availability; alters microbial substrate use efficiency	Cumulative N_2O emissions reduced by ~20%; buffers emission pulses triggered by rewetting	(Yang et al. 2017)
Elevated atmospheric CO_2	C	Suppresses rhizosphere priming effect (significant even at higher application rates), though suppression is weaker than under ambient CO_2	Mitigates excessive decomposition of pre-existing soil organic carbon	(Pei et al. 2020)
	N	Redistributes N from recalcitrant heavy fraction to plant-accessible light fraction; stabilizes particulate organic N within micro-aggregates; metagenomic suppression of genes for N assimilation, nitrification, and nitrate reduction	Increases grain N accumulation by 55.4%; alleviates CO_2 -induced N limitation	(Yang et al. 2026)

use efficiency by 11–39% (Chen et al. 2025b) and by shifting microbial communities toward K-strategist assemblages such as fungi and Actinobacteria that exhibit lower metabolic responsiveness to temperature increases (Chen et al. 2021a). Aged biochar exhibits an even stronger Q_{10} -lowering effect, particularly at lower temperatures, suggesting that this temperature-buffering function for rhizosphere carbon may intensify over time as biochar ages in the root zone (Fang et al. 2014b, 2017). Similarly, under drought or wetting–drying cycles, biochar buffers rhizosphere carbon against destabilization (Liu et al. 2022b). Specifically, biochar's porous structure protects microbes from rewetting stress, reducing CO_2 bursts (Rhymes et al. 2026). Meanwhile, biochar adsorbs root-derived carbon, preventing its rapid mineralization (Weng et al. 2022). It also promotes soil aggregation, physically shielding organic carbon from moisture fluctuations while the retained moisture stabilizes SOC decomposition rates (Pan et al. 2026). Together, these biochar-mediated actions stabilize rhizosphere carbon under drying-rewetting cycles. Moreover, even under elevated CO_2 (Table 4), biochar addition still significantly reduced the rhizosphere priming effect relative to unamended soil, and the magnitude of this suppression increased with increasing biochar application rate, demonstrating that biochar can still mitigate the decomposition of pre-existing soil organic carbon in a future CO_2 -enriched atmosphere, although the suppressive effect was weaker than that observed under ambient CO_2 (Pei et al. 2020).

5.2 Nitrogen cycle

Biochar mediates rhizosphere nitrogen cycling by modifying soil physicochemical conditions, reshaping microbial community structure, and regulating functional gene expression (Craswell et al. 2021; Zhang et al. 2024b). Among the factors controlling these effects, biochar feedstock and pyrolysis temperature are the dominant ones. Wood-based biochar with high porosity improves soil aeration and alters the abundance of functional genes associated with ammonia oxidation, while crop residue biochar with higher available nutrient contents more strongly regulates nitrogen-fixing and denitrifying microorganisms. High-temperature alkaline biochar produced above 400 °C optimizes soil pH for nitrifiers and denitrifiers, while low-temperature biochar with high volatile organic compound contents produces more context-dependent microbial responses (Cao et al. 2021; Zhang et al. 2021). Biochar also regulates rhizosphere nitrogen cycling via modification of root functional traits. It promotes maize root growth and branching to expand the root–soil contact area, increases soybean flavonoid secretion to promote rhizobial nodulation and biological

nitrogen fixation, and maintains stable root exudate dynamics via adsorption to regulate microbial nitrogen transformation activity (Cheng et al. 2018; Cui et al. 2024).

Microbial functional shifts are the core mechanistic link between biochar amendment and rhizosphere nitrogen cycling. For biological nitrogen fixation, crop-based biochar shows stronger promotional effects than wood-based biochar, with effects dependent on baseline soil nitrogen fixation potential and pH (Craswell et al. 2021; Yu et al. 2024). For nitrification, biochar combined with nitrogen-phosphorus-potassium (NPK) fertilizer increases soil potential nitrification rate, with ammonia-oxidizing bacteria (AOB) as the key drivers, while ammonia-oxidizing archaea (AOA) show stronger substrate dependence (Sun et al. 2021). For denitrification, high C/N (>30) alkaline biochar increased *nosZ* abundance by 13.2% and reduced N_2O emissions by 76.7%, as redox-active functional groups on biochar act as electron shuttles to improve the completeness of denitrification (Yuan et al. 2017; Zhang et al. 2024b).

Biochar effects on nitrogen use efficiency and loss pathways show strong context dependence. ^{15}N tracer studies show that biochar can increase plant nitrogen recovery by promoting root uptake, while excessive application may inhibit uptake via lateral root growth suppression (Craswell et al. 2021; Shi et al. 2024). Meta-analyses show that biochar reduces nitrogen leaching by 10.9%, and inhibits ammonia volatilization via NH_3 adsorption by OCFGs and nitrification regulation (Yu et al. 2024). However, long-term application (>3 years) may increase N_2O emissions and nitrogen leaching due to the declining adsorption capacity of aged biochar, and high-temperature alkaline biochar may increase ammonia volatilization risk from urea fertilizer (Craswell et al. 2021; Zhang et al. 2021).

The stability of biochar-mediated rhizosphere nitrogen cycling buffering is challenged by shifts in water regimes, atmospheric CO_2 concentrations, and rising temperatures. As with carbon cycling, biochar demonstrates a capacity to maintain functional stability under these climatic stressors. Under experimental warming, high biochar application rates have been shown to suppress the warming-induced stimulation of N_2O emissions in tropical soils (Rittl et al. 2021). Frequent drying-wetting cycles in irrigated arid agricultural soils profoundly alter rhizosphere nitrogen dynamics, and biochar-rhizosphere interactions represent a critical mechanism to mitigate nitrogen losses and N_2O emissions under these fluctuating hydrological conditions. Specifically, biochar modulates rhizosphere nitrogen cycling by adsorbing ammonium, reducing nitrate availability, and altering microbial substrate utilization efficiency, leading to ~20%

lower cumulative N_2O emissions and buffering the sharp emission flushes triggered by rewetting events (Yang et al. 2017). Under elevated CO_2 , biochar redistributes soil nitrogen from recalcitrant heavy fraction pools to more plant-accessible light fraction pools and promotes the formation of micro-aggregates that physically stabilize particulate organic nitrogen, thereby enhancing nitrogen bioavailability. Metagenomic analysis reveals that biochar suppresses the upregulation of key nitrogen-cycling genes associated with assimilation, nitrification, and nitrate reduction that would otherwise be stimulated under elevated CO_2 , while synergistically increasing plant uptake of both fertilizer-derived and native soil-derived nitrogen, ultimately leading to a 55.4% increase in grain nitrogen accumulation and effective mitigation of CO_2 -induced nitrogen limitation (Yang et al. 2026).

5.3 Phosphorus cycle

Biochar exerts variable effects on rhizosphere phosphorus availability, with net outcomes reflecting the dynamic balance between phosphorus mobilization and immobilization processes. A 10-year paddy field trial showed that annual biochar application reduced rhizosphere phosphorus flux by 11.6% to 79.0% with increasing application rates, indicating progressive phosphorus immobilization under high-dose long-term inputs (Yuan et al. 2024). In contrast, cattle manure biochar increased Olsen P in alkaline desert soil by 134% in the rhizosphere, showing net mobilization effects under specific edaphic conditions (Fan et al. 2023). These divergent responses are primarily driven by biochar properties, soil type, and application duration (Zhang et al. 2025a). Beyond the cycling of inorganic phosphate, biochar also influences the fate of dissolved organic phosphorus (DOP) in the rhizosphere. DOP compounds, including inositol phosphates, nucleic acids, and phospholipids, constitute a substantial fraction of total soil phosphorus and require enzymatic hydrolysis by phosphatases to become plant-available. Biochar application can enhance DOP mineralization by stimulating the activity of phosphatases such as acid phosphomonoesterase (AcP), alkaline phosphomonoesterase (ALP), and phosphodiesterase (PD), which catalyze the hydrolysis of monoesters and diesters to release plant-available orthophosphate. The stimulation of phosphatase activity is often accompanied by shifts in the abundance and community composition of phosphatase-harboring microorganisms, particularly those carrying *phoD* genes, which govern the conversion of organic phosphorus to inorganic orthophosphate (Liu et al. 2024c). Simultaneously, biochar surfaces can adsorb DOP compounds through ligand exchange and electrostatic interactions, temporarily retaining organic phosphorus in the rhizosphere and reducing its leaching loss.

Soil pH and interactions with Fe, Al, and Ca mineral phases are the core chemical mechanisms regulating biochar effects on phosphorus cycling. In acidic soils, the liming effect of biochar reduces Fe^{3+} - and Al^{3+} -driven phosphorus fixation, promoting phosphorus desorption and dissolution to increase plant-available phosphorus (Zhang et al. 2022). In alkaline soils, increased Ca^{2+} activity promotes calcium-bound phosphorus (Ca-P) precipitation, reducing phosphorus availability under high-dose long-term application, as supported by the 10-year paddy trial showing a shift of soluble phosphorus to Ca-P and residual pools (Yuan et al. 2024). In flooded systems, biochar modifies Fe redox status to alter the dissolution of Fe-bound phosphorus, with effects dependent on soil baseline conditions (Li et al. 2021b; Weihrauch And Opp 2018). Biochar surfaces also provide inherent phosphorus adsorption–desorption capacity. Low biochar application rates support short-term phosphorus supply via desorption, while high application rates may immobilize phosphorus into a stable slow-release pool (Luo et al. 2023; Mahmoud et al. 2020).

Biochar also regulates phosphorus cycling via microbial and root-mediated pathways. It provides protected habitat for phosphorus-transforming microorganisms, stimulates phosphorus-solubilizing taxa and phosphatase production, and alters the abundance of phosphorus transformation functional genes (e.g., *phoD*), promoting the mobilization of insoluble phosphorus via organic acid release and enzymatic mineralization (Bornø et al. 2018; Fan et al. 2024). In addition, biochar can promote rice root growth and citrate secretion, upregulate phosphorus transporter gene expression, and enhance phosphorus acquisition under phosphorus-limited conditions (Zhang et al. 2022). Overall, while biochar often increases phosphorus availability, long-term high-rate application in alkaline or flooded systems may reduce availability via fixation and precipitation, and more long-term studies are needed to clarify its coupling with nitrogen and sulfur cycles (Hou et al. 2024; Yuan et al. 2024).

5.4 Sulfur cycle

Biochar modifies sulfur availability in the soil–plant system through shifts in rhizosphere pH, dissolved oxygen, microbial community structure, and root metabolic activity (Fig. 7) (Zhang et al. 2014). A notable pot experiment in calcareous soil showed that dairy manure biochar applied at 0.5% to 2% increased maize growth and chlorophyll content, with optimal performance when combined with a medium sulfate input of 50 mg kg^{-1} . When the biochar rate increased to 5%, soil pH rose to approximately 8.5, and excessive alkalinity reduced plant growth and microbial activity, while decreasing plant-available sulfur (Zhao and Zhang 2021). Biochar can also

regulate sulfur cycling through shifts in the plant metabolome that alter the recruitment and activity of sulfur-cycling microorganisms. In wheat systems, biochar from different feedstocks and application rates altered amino acid metabolism and shifted cysteine and methionine synthesis pathways, with downstream effects on secondary metabolites such as flavonoids, alkaloids, and terpenoids. These metabolites can act as signaling compounds in plant–microbe interactions and can influence the abundance of sulfur oxidizers and sulfate reducers in the rhizosphere. Network analysis from this study also suggests that biochar can increase positive associations and modularity among co-occurring microbial groups (Yang et al. 2025a). Across published studies, biochar feedstock often exerts a stronger control on sulfur cycling outcomes than application rate, which indicates that effects depend on both the inherent sulfur content and surface chemistry of the biochar.

Long-term paddy field evidence suggests that high-dose repeated biochar application can reduce sulfur flux in the rhizosphere. After 10 years of annual application, increasing biochar rates were associated with lower rhizosphere dissolved oxygen and higher soil pH. These conditions promoted sulfate reduction to sulfide and the conversion of soluble inorganic sulfur into calcium-bound and residual forms, which can reduce plant-available sulfur over time (Yuan et al. 2024). Biochar effects on rhizosphere enzyme activity also contribute to sulfur cycling regulation. Low biochar application rates can increase the activity of catalase, urease, and sucrase that correlate with sulfur transformation efficiency, while high rates can inhibit these enzyme activities (Zhao and Zhang 2021). In summary, biochar regulation of sulfur cycling reflects the combined effects of soil chemistry shifts, root metabolic changes, microbial functional modifications, and multi-element coupling. Short-term moderate-rate biochar application with appropriate sulfate input can increase plant-available sulfur by maintaining suitable pH and active microbial processes, while long-term high-rate application can reduce availability through over-alkalinity, low dissolved oxygen, and sulfur immobilization (Zhao and Zhang 2021). Future work should use integrated multi-omics and long-term field designs to link root metabolite shifts with sulfur-cycling functional microbes and sulfur speciation outcomes in the rhizosphere (Yang et al. 2025a).

5.5 Iron cycle

Biochar influences rhizosphere iron cycling by modifying Fe redox transformation, iron plaque formation on root surfaces, and Fe mineral evolution, and these changes can alter both contaminant mobility and plant iron nutrient availability (Fig. 7) (Si et al. 2024a; Xu et al. 2024a).

These effects arise through coupled physicochemical regulation, microbial community selection, and interfacial mineral transformation processes. Biochar sets key boundary conditions for Fe cycling by shifting rhizosphere pH, CEC, and carbon availability, which regulates Fe adsorption and transformation pathways (Si et al. 2024a, 2024b; Xu et al. 2024c). A well-documented example shows that co-pyrolyzed peanut shell and corn stover biochar increased soil pH to 6.36 and CEC to 15.34 cmol(+) kg⁻¹, which supported enhanced Fe-related transformation processes in the tested soil (Xu et al. 2024c). Across multiple studies, co-application of biochar with AMF or PGPR can further increase rhizosphere dissolved organic carbon and provide energy sources for Fe-cycling microorganisms, which can increase available Fe through complexation and activation of mineral-bound Fe. Microbial regulation is central to biochar-mediated Fe cycling, as biochar provides protected habitat and carbon sources and can selectively enrich Fe-metabolizing taxa. A key study found that corn stover biochar increased the abundance of *Geobacter* and *Clostridium* by 43% and 73% respectively, and these Fe-reducing bacteria can use labile carbon from biochar as an electron donor and promote the reduction of Fe(III) to Fe(II), increasing dissolved Fe concentrations in soil pore water (Xu et al. 2024a). A complementary study found that the same co-pyrolyzed peanut shell and corn stover biochar increased Fe-oxidizing groups and supported iron plaque formation on root surfaces through Fe(II) oxidation, with abundance patterns linked to soil pH and cadmium speciation changes (Xu et al. 2024c). Fe redox cycling is the core mechanism linking biochar amendment to Fe speciation and iron plaque formation. Biochar can enhance Fe(III) reduction and Fe(II) migration within the soil matrix, and at root surfaces Fe(II) can be oxidized through radial oxygen loss (ROL) to form iron plaque. Alternative pathways such as nitrate reduction coupled with Fe(II) oxidation can promote Fe and Mn oxide formation and increase oxide-bound cadmium fractions in contaminated soils (Si et al. 2024a, 2024b). A key quantitative example shows that Fe-modified sewage sludge biochar increased Fe content in root surface plaque to 12.8 g kg⁻¹, a 67% increase compared with the unamended control, and cadmium adsorption in the plaque also correlated positively with Fe content with a correlation coefficient of 0.83 and $P < 0.001$ (Huang et al. 2023). These results support the concept that biochar can reduce heavy metal translocation to plant tissues by strengthening Fe plaque and Fe oxide sinks at the root–soil interface. Biochar regulation of Fe cycling is strongly environment-dependent. In acidic cadmium-contaminated paddy soil, the anion type in Fe-modified biochar can shift whether regulation is dominated by Fe(III) reduction or Fe(II) oxidation,

which alters the balance between iron plaque formation and amorphous Fe oxide accumulation (Si et al. 2024a). In neutral soils, biochar combined with ZVI has been reported to increase the Fe cycling rate by 53% through coupled ZVI redox reactions and biochar electron shuttling, which improved heavy metal immobilization compared with single amendments (Si et al. 2024b).

5.6 Other nutrient and beneficial element cycles

Biochar regulates the availability of potassium, sodium, calcium, magnesium, and silicon through a set of shared core processes. These processes include direct input of soluble and exchangeable forms of these elements, modification of rhizosphere pH and CEC, regulation of adsorption–desorption equilibria on soil and biochar surfaces, and reshaping of pore structure and microbial activity that control ion transport to plant roots. Net outcomes depend on biochar feedstock, pyrolysis temperature, application regime, soil properties, and aging dynamics (Gondek et al. 2019).

For potassium (K), wheat straw biochar produced at 700 °C increased soil available K from nearly 20 mg kg⁻¹ to 300 mg kg⁻¹, as high-temperature pyrolysis enriches inherent K content in biochar and enhances its mobility. Biochar can retain K in the topsoil to reduce leaching and improve K fertilizer use efficiency. Repeated low-rate application combined with NPK nitrogen–phosphorus–potassium fertilizer outperforms one-time high-rate input for sustained K availability (Bao et al. 2024; Latini et al. 2019).

For sodium (Na), biochar regulates Na availability via direct input, surface adsorption, and CEC-mediated retention. Under salt stress, biochar can reduce exchangeable Na and improve the K⁺/Na⁺ balance to alleviate salt toxicity, even when soluble Na pools increase. However, high-Na feedstock biochar may elevate soil soluble Na content, with net agronomic outcomes dependent on plant salt sensitivity and soil buffering capacity (Fernandes et al. 2018; Gondek et al. 2019; Latini et al. 2019; Rasuli et al. 2022; Wang et al. 2019b).

For calcium (Ca) and magnesium (Mg), manure-derived biochar provides high Ca and Mg inputs, raises soil base saturation, and shifts Ca and Mg speciation toward plant-accessible pools via its liming effect, especially in highly weathered acidic soils. Co-application of biochar with compost increased extractable Ca from 112 mg kg⁻¹ to 5021 mg kg⁻¹ in an Ultisol, as organic functional groups enhance Ca desorption and biochar liming expands the accessible Ca pool (Berek et al. 2018; Gondek et al. 2019; Mahmoud et al. 2020). Ca binds more strongly to cation exchange sites than Mg and Na, reducing Mg leaching risk, while Mg release from biochar shows strong pH sensitivity, with 19.8 times higher

release under acidic conditions than alkaline conditions (Fernandes et al. 2018; Kypridou et al. 2022; Latini et al. 2019; Rasuli et al. 2022; Wei et al. 2013).

For silicon (Si), Si-rich feedstock (e.g., rice straw) biochar is a key regulator of the soil Si cycle. Biochar produced at 550 °C had a total Si content of 78.2 g kg⁻¹, nearly 2.5 times that of raw rice straw, with higher proportions of easily soluble silicic acid (H₄SiO₄) and adsorbed silicate fractions that constitute plant-available Si (Yao et al. 2022). The carbon-silicon coupling framework formed during pyrolysis reduces rapid Si leaching to enable sustained slow release, while Si protects carbon from microbial decomposition to maintain long-term pool stability. Biochar-derived silicic acid and organically bound Si can also support aluminosilicate formation for aluminum detoxification and enhance plant stress resistance (Muhammad et al. 2016; Wang et al. 2019b).

Across all elements, biochar effects are conditional rather than universal. Agronomic benefits are consistent when biochar type and pyrolysis conditions are matched to target soil and crop needs, including K supply and retention, Na toxicity mitigation, Ca and Mg nutrition improvement, and Si-mediated stress protection. Long-term performance depends on topsoil nutrient retention, moderate repeated inputs, and management of trade-offs among cation competition, leaching risk, and soil buffering capacity (Muhammad et al. 2016; Murtaza et al. 2023).

6 Ecological functions of the biochar rhizosphere system

6.1 Signal transduction and information exchange

Biochar modulates rhizosphere signal transduction through multiple pathways, including adsorption of microbial signaling molecules, regulation of plant hormone metabolism, reshaping of ion homeostasis, modulation of root metabolite secretion, and synergistic interactions with beneficial rhizosphere microorganisms, which jointly shape plant growth, nutrient use efficiency, and stress resistance (Masiello et al. 2013; Sarfraz et al. 2019; Wan et al. 2025). Quorum sensing signals are central to rhizosphere microbial communication, and biochar adsorption of these signals has been directly verified in multiple studies. Biochar can bind N-acyl homoserine lactones (AHLs) secreted by Gram-negative bacteria, and this adsorption capacity tends to increase with rising pyrolysis temperature. For example, biochar produced at 700 °C had a much higher specific surface area than biochar produced at 300 °C, increasing the inhibition efficiency of AHL-mediated communication by approximately one order of magnitude (Masiello et al. 2013). Biochar also reshapes rhizosphere microbial community structure

and interaction networks. Across agricultural systems, biochar commonly increases microbial diversity and network complexity, enriches functional groups such as denitrifiers, and suppresses some undesirable groups such as methanogenic archaea. Under plastic film mulching, biochar optimized colonization patterns in the maize rhizosphere and enriched genera such as *Sphingomonas* and *Bradyrhizobium*, further reconfiguring inter-microbial information exchange (Sui et al. 2023). Biochar also reduces allelopathic pressure in the rhizosphere by adsorbing phenolic compounds or inhibiting their secretion from plant roots. In a continuous ginseng cropping system, multiple biochar products reduced rhizosphere phenolic acid concentrations, suppressed pathogens such as *Fusarium* and *Ilyonectria*, increased beneficial microorganisms such as AMF and *Bryobacter*, and improved plant growth and quality traits (Liu et al. 2022a). Biochar further inhibits soil-borne pathogens partly by inducing plant systemic resistance, as demonstrated in tomato and rice systems, where biochar increased the expression of defense-related genes and signaling pathways and increased H_2O_2 accumulation, contributing to the suppression of root-knot nematodes (Arshad et al. 2024). Synergy with PGPR can further strengthen rhizosphere signaling and defensive function. Biochar provides protected microhabitats that reduce PGPR population loss, while PGPR can enhance glomalin production and plant carbon allocation to improve soil aggregation, nutrient cycling, and soil carbon sequestration (Sarfranz et al. 2019). Plant hormone signaling is a major control point for rhizosphere responses to biochar amendment, with effects depending on irrigation regimes and microbial partners. In maize, wheat straw biochar combined with partial root zone drying increased abscisic acid (ABA) concentration in xylem sap, while in drought-stressed chickpea, co-application of corn stover biochar and *Paenibacillus lentimorbus* increased indole-3-acetic acid (IAA), cytokinin (CK), and salicylic acid (SA) levels, maintained stable jasmonic acid (JA) levels, and shifted xylem ion profiles toward higher K^+ , Ca^{2+} , Mg^{2+} , NO_3^- , and PO_4^{3-} with lower Na^+ , thereby supporting ion homeostasis and water use efficiency (Liu et al. 2024a; Wan et al. 2025). Biochar regulation of hormone and stress metabolite profiles is crop- and context-dependent. In sugarcane, biochar amendment enriched zeatin, melatonin, phenyllactic acid, and sucrose in plant tissues, and these changes correlated with the abundance of beneficial bacteria such as *Bradyrhizobium*, which improved soil nitrogen forms and enzyme activities and promoted sugar accumulation. Under drought stress, walnut shell biochar optimized tomato root architecture and reduced ABA and

proline accumulation in plant tissues. In cacao systems, in-row placement of biochar-based fertilizer increased plant biomass, leaf area, and foliar P concentration, outperforming alternative placement methods (Fallah et al. 2023; Zhang et al. 2025b). In the *Fusarium* wilt system, biochar induced systemic resistance by shifting defense signaling pathways, upregulating JA biosynthesis and signaling genes including *LOX*, *AOS*, and *JAR1*, affecting auxin and brassinosteroid pathways, downregulating SA pathway genes including *PAL* and *PR1*, and promoting lignin and flavonoid synthesis to reduce disease incidence and improve photosynthetic performance (Jaiswal et al. 2020).

Biochar can also act as a Ca^{2+} source and trigger Ca^{2+} -dependent defense signaling cascades, thereby activating sensor proteins such as CaM, CBL, and CDPKs, regulating the expression of stress-related genes including those encoding glutathione S-transferase (GST), ascorbate peroxidase (APX), catalase (CAT), and ACC oxidase (ACO), and strengthening plant structural defense and antioxidant capacity (Bisht et al. 2024; Sarfranz et al. 2024). At the molecular scale, biochar can promote growth-related signaling while downregulating specific defense programs, suggesting a modulation of the plant growth-defense trade-off. In *Arabidopsis* and lettuce, biochar upregulated auxin and brassinosteroid-related genes such as *IAR3*, *ILL6*, *DWF4*, and *CYP72C1*, promoted cell wall loosening genes such as *XTH9* and expansins, and simultaneously downregulated JA synthesis genes including *LOX2* and *AOS* and defense-related genes such as *PDF1.2* and *THI2.1* (Viger et al. 2015). Biochar also strengthens rhizosphere signal exchange by regulating root carboxylate secretion. In barley, carboxylate release correlated with biochar ash, P, and Mg content and predicted plant biomass response to amendment. In maize under reduced nitrogen input, corn stover biochar upregulated *ZmMATE1* and increased the secretion of specific metabolites, which correlated with soil NH_4^+ -N and total P concentrations and mitigated plant biomass loss (Cheng et al. 2018; Honvault et al. 2022). Biochar-derived humic-like substances can alter root signal perception, reducing root hair length and density in *Arabidopsis* even under phosphorus starvation, indicating that regulation occurs through signal perception rather than direct nutrient supply (Graber et al. 2015). Biochar can also reprogram root metabolomes and secondary metabolite profiles, with effects dependent on application rate and feedstock, and moderate rates often producing stronger regulatory effects in some systems and plant roots tending to proliferate toward biochar particles. Long-term biochar application can shift rhizosphere metabolites and microbiomes toward higher disease suppression capacity and crop yield (Prendergast-Miller et al. 2014).

6.2 Plant biotic stress alleviation

Biochar can improve soil health while suppressing plant diseases across diverse crop-pathogen systems, including soil-borne and air-borne diseases, parasitic nematodes, and some virus-mediated diseases. Its core value lies in multi-pathway regulation of plant-soil-microbe-protist-pathogen-vector interactions rather than a single mode of action, thereby supporting reduced reliance on chemical fungicides (Bhatt et al. 2024). Biochar physico-chemical properties such as pH, CEC, and porosity support disease suppression, while feedstock type, pyrolysis temperature, and modification shape its functional specificity. For instance, it can enrich beneficial taxa such as *Pseudomonas* and *Trichoderma* by providing protected microhabitats and growth substrates (Jin et al. 2022). Representative agricultural systems show combined top-down and bottom-up disease control by biochar. In continuous cropping soil, rice husk biochar combined with a *Bacillus* synthetic community increased beneficial bacterial abundance, reduced *Ralstonia* populations, promoted predatory protists, and suppressed *Fusarium oxysporum* to increase plant biomass. In tomato systems, biochar enriched a *Pseudomonas* strain that directly antagonized *Fusarium* and activated plant defense signaling to reduce wilt severity, while its pores can also host beneficial *Bacillus* strains and suppress oomycete pathogens such as *Pythium* (Bhatt et al. 2024; Jin et al. 2022). Biochar can also contribute direct pathogen inhibition through pyrolysis-derived volatile organic compounds, and through selective inhibition by toxic constituents that shift rhizosphere microbial community structure, thereby increasing AMF root colonization and reducing *Fusarium*-related root diseases in some crop species (Hou et al. 2022). Biochar can induce both induced systemic resistance and systemic acquired resistance in plants, enhancing the accumulation of phenolics, flavonoids, antioxidant enzymes, and pathogenesis-related proteins to reduce disease severity. In pepper systems, rice straw biochar increased leaf phenolic and flavonoid content and improved catalase and peroxidase activity, and it showed direct antimicrobial activity against pathogens in vitro (Hou et al. 2022). For plant-parasitic nematodes, biochar effects often reflect induced plant resistance rather than direct toxicity, as demonstrated by multiple biochar products reducing lesion nematode infestation in carrot systems, and oak wood biochar reducing root-knot nematode infestation in rice at moderate application rates. For virus-mediated diseases, biochar effects can be indirect, operating through the suppression of insect vector populations (Singh et al. 2022). Biochar can shift root exudate profiles to favor beneficial chemotaxis and biofilm formation, thereby supporting the colonization of beneficial microorganisms

and defense signaling activation, while also improving overall soil conditions and adsorbing pathogen toxins and cell wall-degrading enzymes to reduce pathogen virulence. Targeted modification can further enhance biochar adsorption capacity and beneficial microbial colonization, but application dose remains critical. Moderate doses are typically optimal, whereas excessive rates risk reduced efficacy through microbial community imbalance or adsorption of applied pesticides (Bhatt et al. 2024; Jin et al. 2022). In summary, biochar achieves enhanced plant disease resistance through the synergistic actions of microbial community remodeling, plant defense activation, soil environment improvement, and modification-enhanced effects, demonstrating significant control effects against fungal, bacterial, nematode, and virus-mediated diseases, as well as continuous cropping obstacles (Fig. 8). However, the field application of biochar still needs to address issues such as dose standardization, crop cultivar compatibility, and modification cost control. Future in-depth exploration of the interaction mechanisms between biochar and protists or virus vectors, together with the functional specificity of differently modified biochar products, will provide more precise technical support for green agricultural disease control.

6.3 Plant abiotic stress alleviation

Abiotic stresses such as drought, salinity, and heavy metal pollution increasingly threaten global crop yields and food security. Biochar can alleviate these stresses through coordinated soil physical improvement, ion homeostasis regulation, redox control, and rhizosphere ecological modulation (Fig. 9) (Sarraf et al. 2024; Zaib et al. 2022). Under salt stress, biochar can reduce soil electrical conductivity, sodium adsorption ratio, and exchangeable sodium percentage, promote excess Na^+ leaching, supply Ca^{2+} and Mg^{2+} to displace exchangeable Na^+ , and improve soil structure and water retention capacity, while in plant tissues, enhancing antioxidant enzyme activity and supporting cellular K^+/Na^+ homeostasis, including the upregulation of ion transporter genes such as *SOS1* and *NHX1* (Ali et al. 2025; Wu et al. 2023). Synergy with PGPR and AMF can amplify plant salt tolerance by improving beneficial microbial establishment, reducing plant Na^+ uptake, lowering stress ethylene levels via 1-aminocyclopropane-1-carboxylate deaminase, and improving ABA-related stomatal regulation, while biochar combined with PGPR can increase the activity of soil enzymes that support nutrient cycling (Malik et al. 2022; Rahim et al. 2025). Under drought stress, biochar can improve soil water holding capacity through its porous structure, reduce soil bulk density, increase total porosity, and optimize the root growth environment, thereby promoting plant osmotic adjustment, enhancing antioxidant defense systems, protecting photosynthetic

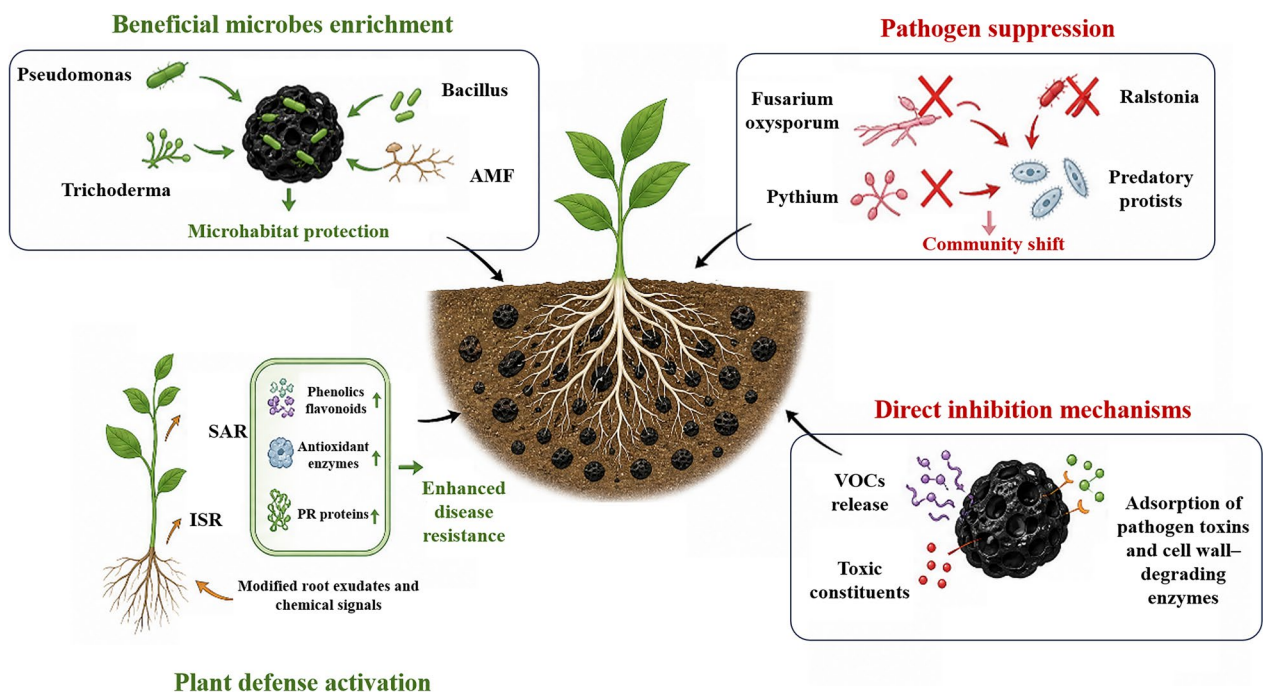


Fig. 8 Mechanisms underlying biochar-mediated regulation of crop biotic stress

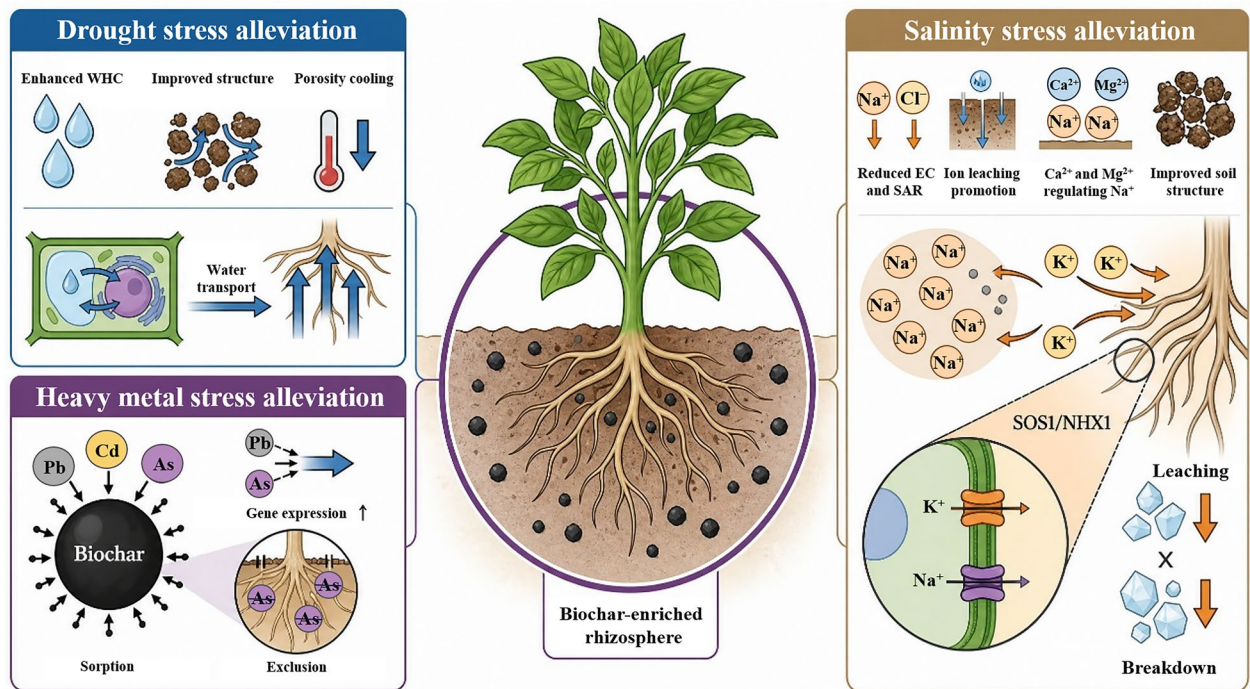


Fig. 9 Mechanisms underlying biochar-mediated regulation of crop abiotic stress

apparatus, and upregulating aquaporin-related genes such as plasma membrane intrinsic proteins, while also lowering soil thermal conductivity and moderating rhizosphere temperature stress; PGPR synergy can further improve root biomass accumulation and plant water use efficiency (Malik et al. 2022; Wu et al. 2023). Under heavy metal stress, biochar can immobilize toxic metals through adsorption and precipitation pathways, reducing plant metal uptake, while increasing pH and CEC and improving plant nutrient uptake to reduce competitive metal absorption. For arsenic contamination, biochar can shift As speciation toward less toxic forms, and PGPR can reduce highly toxic Cr(VI) to less mobile Cr(III), with biochar also upregulating antioxidant and metal tolerance genes in some crop species (Etesami et al. 2025; Rahim et al. 2025). At the molecular level, biochar can upregulate the expression of antioxidant enzyme genes such as *OsSOD*, *OsPOD*, and *OsCAT*, and metal tolerance genes such as *OsFSD1*, thereby enhancing plant detoxification capacity for heavy metals (Sarraf et al. 2024).

Biochar regulation of rhizosphere micro-ecology is a core pathway for abiotic stress alleviation. It serves as a stable carbon source to promote the proliferation of beneficial microorganisms, increase soil microbial diversity and activity, and facilitate the colonization of nitrogen-fixing bacteria, phosphorus-solubilizing bacteria, and AMF (Malik et al. 2022; Zaib et al. 2022). Aged biochar surfaces undergo oxidation to form more oxygen-containing functional groups, strengthening interactions with soil microorganisms. Furthermore, compared to large particle biochar, nano biochar can better optimize rhizosphere microbial community structure by regulating the composition of root exudates (Sarma et al. 2024). Synergy between biochar and PGPR can upregulate the expression of plant defense genes such as *PR1a* and *PI2*, induce systemic resistance through the jasmonic acid/ethylene signaling pathway, achieve high inhibition efficiency against pathogens such as *Fusarium* and root-knot nematodes, and further enhance antioxidant defense capacity by regulating plant redox balance via the ascorbate–glutathione cycle (Etesami et al. 2025; Mushtaq et al. 2024). Furthermore, biochar improves soil aggregate stability by increasing the number of macro-aggregates larger than 2 mm, reducing the proportion of micro-aggregates smaller than 0.25 mm, increasing the mean weight diameter of aggregates, and enhancing soil erosion resistance (Chi et al. 2024).

7 Biochar life cycle assessment, economic feasibility, and environmental risks

7.1 Life cycle assessment and economic feasibility

Life cycle assessment (LCA) provides a systematic framework for evaluating the net environmental consequences of biochar systems from feedstock sourcing to field

application (Lehmann et al. 2021). Biochar-mediated carbon dioxide removal has substantial technical potential, although the magnitude of climate benefits depends on feedstock scenarios and system implementation. Using only forest or crop residues, biochar can achieve approximately 10% of the required carbon dioxide removal for 1.5 °C pathways and about 25% for 2 °C pathways, increasing to 15–35% and 35–50%, respectively, when dedicated energy crops are included as feedstocks (Tisserant And Cherubini 2019). An early foundational LCA study analyzing corn stover, yard waste, and switchgrass demonstrated that biochar systems are financially viable as a distributed system using waste biomass (Roberts et al. 2010). The environmental performance is shaped by pyrolysis conditions, soil properties, and field management practices (Tisserant And Cherubini 2019). Among production technologies, gasification exhibits superior economic attributes compared to pyrolysis and hydrothermal carbonization, while feedstock type plays a predominant role in determining biochar properties (Li et al. 2024b). Potential trade-offs between environmental impacts, including particulate matter formation, acidification, and eutrophication, depend on the background energy system and whether residues or dedicated feedstocks are used (Tisserant And Cherubini 2019). Deployment context significantly shapes the overall performance of biochar systems. Mobile biochar production, which uses forest residues that would otherwise be pile-burned, reduces global warming potential by 1.9–2.8 tCO₂e per tonne of biochar across three portable pyrolysis systems (Puettmann et al. 2020). Co-locating biochar production facilities with anaerobic digestion plants minimizes feedstock transport distances, and in the United Kingdom context, the resulting biochar delivers net emissions reductions of 1.15–1.20 tCO₂e per tonne of biochar with an 88% stable carbon fraction (Gameralalage et al. 2025).

Biochar systems are economically complex and multifaceted. A cost–benefit analysis spanning application rates from 4 to 28 t ha^{−1} estimated total production costs at \$233 t^{−1}, with labor accounting for 27.1% of production and application expenses (Patel And Panwar 2024). A systematic review concluded that profitability is highly uncertain and case-specific, depending on location, feedstock type, scale of operation, pyrolysis conditions, biochar price, cultivated crop, and the potential internalization of externalities (Campion et al. 2023). Economic outcomes vary markedly across different agricultural contexts. In a cost–benefit analysis across two contrasting geo-economic settings, biochar application had a positive net present value for cereal cropping in Sub-Saharan Africa when the yield effect extended for 30 years, whereas all North-Western European scenarios showed

negative net present values even over an indefinite time horizon, with grain yield improvements of from +0.07 to +0.28 t ha⁻¹ yr⁻¹ in North-Western Europe and +0.18 to +1.00 t ha⁻¹ yr⁻¹ in Sub-Saharan Africa (Dickinson et al. 2015). In rice production systems, benefit–cost ratios of biochar-amended fields were below 1 in the first cropping season but rose to between 1.22 and 1.84 in the second cropping season due to the residual effect of biochar (Danso et al. 2023).

Despite considerable academic enthusiasm, the economic reality of biochar deployment remains sobering. Feedstock costs can comprise up to 75% of production expenses, rendering systems viable only with access to free residues or monetized carbon credits (Gristina And Scalenghe 2026). Overall, biochar application in soils presents relatively low risks of negative environmental impacts and can also improve soil quality when feedstock mix and pyrolysis conditions are optimized (Tisserant and Cherubini 2019). Translating these agronomic advantages into economic viability, however, requires carbon credit monetization, economies of scale, and policy mechanisms that convert environmental benefits into tangible financial incentives for farmers (Campion et al. 2023; Gristina And Scalenghe 2026).

7.2 Potential environmental risks

7.2.1 Biochar nano-colloid formation and mobility

A critical but underappreciated secondary risk of biochar application arises from the physical disintegration of bulk biochar into micro- and nano-scale colloids during field aging. Biochar colloids originate from fine fractions produced during pyrolysis or are generated through post-application weathering involving physical, chemical, and biological fragmentation (Gui et al. 2021; Zhang 2025). Biochar colloids exhibit high colloidal stability under environmentally relevant conditions and can travel through soil profiles or in runoff, potentially transporting sorbed contaminants or nutrients over long distances (Gui et al. 2021). Formation is driven by initial production of nano-scale particles and subsequent fragmentation, while stability depends on surface charge, ionic strength, cation valence, natural organic matter interactions, and hetero-aggregation with soil minerals (Song et al. 2019). A central controversy exists in that while biochar colloids can immobilize pollutants and enhance nutrient retention in situ, their mobility may facilitate contaminant migration and carbon loss from the target soil horizon (Xie et al. 2026). Chemical aging substantially increases the mobility of biochar colloids in porous media by increasing the abundance of negatively charged oxygen-containing functional groups on colloid surfaces, thereby enhancing electrostatic stabilization and transport potential (Wang et al. 2019c). Compared

to pristine biochar, aged nano-biochar exhibited higher dispersion stability due to a more negative zeta potential and increased specific surface area and mesoporous volume (Wang et al. 2019c). The rhizosphere, with its high concentrations of organic acids and intense microbial activity, may accelerate biochar fragmentation and colloid generation compared to bulk soil, as suggested by the well-documented chemical weathering of biochar by organic acids and the role of microbial processes in the physical breakdown of soil organic matter; both processes raise the possibility that similar fragmentation processes are intensified in the rhizosphere (Wang et al. 2016). Once formed, nano-biochar exhibits better dispersion and stronger migration ability than bulk biochar in soil environments, and pollutants associated with nano-biochar may disperse further in soil as a result. Beyond its potential to exert adverse ecotoxicological impacts on soil fauna, nano-biochar also alters soil microbial and enzymatic activities, plant growth, and physicochemical properties (Zhang 2025).

7.2.2 Contaminant co-transport, groundwater risk, and endogenous pollutant hazards

Building on the above understanding of nano-colloid behavior, direct experimental evidence has confirmed that these colloids facilitate the downward transport of contaminants along the soil profile, posing a potential risk to groundwater quality. Biochar colloids derived from wood chip and wheat straw at two pyrolysis temperatures were shown to facilitate the transport of Cr(VI) in a loam clay Ultisol by 0.5–7.0 times compared to systems without biochar colloids, with the enhancement attributed to competition between biochar colloids and Cr(VI) for available sorption sites on soil surfaces (Chen et al. 2022a, 2022b). Similar co-transport risks have been documented for other heavy metals, with biochar colloids acting as carriers for Cd²⁺ to considerably facilitate its transport, mainly due to strong binding affinities of colloids toward Cd²⁺ and the high mobility of colloids in porous media (Zhang et al. 2024c). Low-molecular-weight aromatic acids, common organic substances in the rhizosphere environment, further promoted biochar colloid mobility and enhanced the contaminant-mobilizing transport capacity of colloids (Pan et al. 2023). These observations lead to the recommendation that risk assessment of biochar-facilitated heavy metal transport should be carefully considered when biochar is applied to the remediation of heavy metal-contaminated sites (Sun et al. 2022). The co-transport of organic contaminants with biochar colloids has also been documented. Column experiments found that biochar colloids mainly acted as a vehicle to facilitate the transport of phenanthrene, atrazine, and oxytetracycline, with dissolved organic

carbon released from biochar colloids also contributing to increased mobility of organic contaminants in dissolved form (Hameed et al. 2020, 2021). These findings collectively demonstrate that colloid-facilitated contaminant transport represents a significant secondary environmental risk that has received insufficient attention in the biochar application literature.

Beyond colloid-mediated transport, biochar can serve as a direct source of environmental contaminants. A comprehensive review categorized biochar-associated risks into endogenous risks, originating from pollutants inherently present in feedstock materials including heavy metals, PAHs, dioxins, volatile organic compounds (VOCs), persistent free radicals, and metal cyanide, and exogenous risks, arising from contaminants adsorbed from the surrounding environment after application (Dong et al. 2025). Biochar produced at high temperatures under oxygen-limited conditions can contain both well-known contaminants and emerging contaminants, whose potential to induce phytotoxicity, cytotoxicity, and neurotoxicity highlights the need for effective contaminant control strategies (Brtnicky et al. 2021; Han et al. 2022). Post-production treatments such as thermal treatment or natural and artificial aging help organic contaminant removal and breakdown, while co-pyrolysis of metal-rich feedstock with metal-free biomass is the primary approach for reducing total potentially toxic element levels (Han et al. 2022). The aging process itself may release previously immobilized contaminants back into the soil solution, as biochar undergoes oxidation and mineral dissolution during long-term field aging, and heavy metals that were initially stabilized through precipitation or complexation may gradually become more labile, particularly under conditions of soil acidification or increased salinity (Mia et al. 2017; Ren et al. 2022). These converging risks from colloid-facilitated transport, endogenous pollutants, and aging-induced contaminant remobilization underscore the need for systematic environmental risk assessment protocols and quality standards for biochar products before field deployment (Dong et al. 2025). Future research should focus on long-term quantification of colloid export from biochar-amended soils, fate assessment of biochar colloids in aquatic systems, and comprehensive evaluation of subtle ecological effects from chronic low-level exposure to biochar-derived contaminants.

8 Research perspectives

8.1 Current research gaps

Most existing studies focus on individual rhizosphere processes such as water retention, heavy metal adsorption, or microbial community shifts, while the synergistic regulatory mechanisms within the multi-interface

biochar–soil–microorganism–root system remain poorly resolved. Three core knowledge gaps stand out. First, the specific interaction mechanisms between biochar surface functional groups and root exudates, mineral ions, or signaling molecules remain unclear, and the cascade pathways linking biochar-driven physical microenvironment remodeling, rhizosphere chemical signal dynamics, and microbial functional responses lack a unified quantitative framework. Second, the dynamic aging mechanisms of biochar and its long-term functional attenuation patterns are not fully characterized, with multi-year field data on aging-driven changes in biochar structure, surface properties, and associated microbial functions remaining limited and pollutant release risks during aging insufficiently assessed. Third, methodological bottlenecks restrict in-depth mechanistic insight. Microscale in situ real-time monitoring of rhizosphere dynamics is scarce, and most data derive from pot experiments or short-term field trials rather than long-term cross-regional positioning studies, a limitation that permeates the mechanistic evidence synthesized in this review. This is particularly acute for high-resolution process studies addressing microbial community succession (Sect. 4) and rhizosphere signal transduction (Sect. 6), where root density is artificially amplified, the rhizosphere volume is compressed, and water and nutrient regimes are tightly controlled, conditions that can exaggerate biochar–microbe–root interactions and distort the ecological functions attributed to biochar. Field validation of the pot-derived mechanisms, including community network rewiring, keystone taxa enrichment, and quorum sensing interference, remains a critical unmet need. Future progress requires field-based in situ monitoring at the millimeter scale of root–biochar–soil interfaces to explicitly test whether these mechanisms operate with comparable significance under natural environmental heterogeneity. Furthermore, interdisciplinary integration remains inadequate to build quantitative mechanistic models linking gene regulation, metabolite dynamics, and rhizosphere environmental variables.

8.2 Future key research directions

To advance from descriptive understanding to predictive capability, we propose a three-tier research framework with clearly defined priorities, each directly linked to specific contradictions and unresolved inconsistencies identified in the preceding sections.

8.2.1 Priority 1 (highest): Resolve the context-dependence of biochar effects on rhizosphere physical and chemical functioning

The manuscript has identified several persistent contradictions that require targeted investigation. Section 2

documents that biochar improves hydraulic conductivity in most soils but reduces infiltration at high application rates, yet the rate threshold at which benefits reverse to detriments remains undefined for different soil textures and biochar particle sizes. Section 3 reveals that biochar simultaneously immobilizes contaminants through sorption and precipitation while its colloidal fractions can facilitate contaminant transport downward, yet the net balance between immobilization and mobilization under field-relevant flow conditions has not been quantified. Section 5.3 highlights that biochar increases phosphorus availability in acidic soils through liming but decreases it in alkaline soils through Ca-P precipitation, yet the soil pH and calcium content boundaries separating these opposing outcomes are not established. Addressing these contradictions requires systematic dose–response experiments that map the transition from benefit to detriment across gradients of application rate, soil texture, and biochar particle size for each target function, paired with mechanistic studies using isotope tracing and synchrotron-based spectroscopy to quantify the competing immobilization and mobilization pathways at the biochar–soil interface.

8.2.2 Priority 2 (high): Systematically characterize biochar aging dynamics and establish quantitative benefit-risk trade-off frameworks

Section 3.2 shows that aging progressively oxidizes biochar surfaces, increasing CEC and nutrient retention while reducing sorption capacity for hydrophobic organic contaminants. Section 7.2 demonstrates that aging generates nano-colloids that facilitate contaminant co-transport, yet the timescale over which the beneficial aging effects peak and the point at which colloidal risks begin to dominate are unknown. Section 3.3 further reveals a functional transition from precipitation-dominated to complexation-dominated metal immobilization as biochar ages, yet the timing and reversibility of this transition across soil types have not been characterized. Coordinated long-term field trials across contrasting soil types and climates, paired with laboratory accelerated aging experiments, are needed to track the co-evolution of surface chemistry, pore structure, colloidal generation rates, and microbial community function over decadal timescales, with the goal of constructing predictive models that define safe application windows by identifying when the net benefit of biochar aging transitions to net risk for each soil-biochar combination.

8.2.3 Priority 3 (medium-term): Resolve the contradictory microbial responses to biochar and build an integrated monitoring framework

Section 4.4 documents that low biochar rates stimulate enzyme activity while high rates inhibit it, and Sect. 4.1 notes that biochar enriches beneficial microbes but

certain feedstocks introduce toxic compounds that suppress sensitive groups, yet the ecological significance of these bidirectional effects, whether the temporary inhibition at high rates or from toxic feedstocks has lasting consequences for rhizosphere function, remains unresolved. Section 6.2 reports disease suppression across diverse pathosystems, but the mechanisms (induced resistance versus direct antagonism versus microbial community shifts) likely vary by system in ways that are not yet predictable. Addressing these gaps requires field-based microbial time-series studies that pair metatranscriptomics with enzyme assays and disease incidence tracking to disentangle transient responses from persistent functional changes, together with the development of microscale in situ monitoring technologies for the root–biochar–soil interface and the establishment of long-term field trials with standardized protocols to provide the data foundation for resolving these inconsistencies and constructing predictive mechanistic models.

9 Conclusions

This review systematically synthesizes the multidimensional regulatory effects of biochar on the rhizosphere, and clarifies its core value in enhancing plant stress resistance and supporting sustainable agricultural production. These effects are driven by the synergistic coupling of physical, chemical, and biological pathways. Physically, biochar optimizes soil structure and water dynamics to support root growth. Chemically, it buffers soil acidity, mediates nutrient cycling, and drives pollutant immobilization via interfacial reactions. Biologically, it reshapes rhizosphere microbial communities by providing protected habitats and enriching beneficial functional taxa. These pathways form an integrated regulatory network to modulate plant growth, nutrient use efficiency, and stress resistance. Biochar shows substantial application potential in alleviating major abiotic stresses including drought, salinity, and heavy metal pollution, and suppressing biotic stresses such as soil-borne diseases and plant-parasitic nematodes. Future advances in this field require targeted design of functional biochar, in-depth mechanistic dissection of biochar–rhizosphere–microbe–plant interactions, standardized application frameworks paired with long-term field monitoring, and comprehensive economic and environmental benefit assessments. Ultimately, precise matching of biochar application strategies to specific soil-crop systems, alongside effective risk and cost control, is essential for the safe, scalable and sustainable deployment of biochar in global agricultural systems.

Supplementary Information

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Supplementary Material 1.

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Author contributions

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Data availability

Data sharing is not applicable to this article as no new data were created or analysed in this review. All sources cited are included in the reference list.

Declarations

Competing interests

Xinde Cao is an EBM of the journal Biochar, and he was not involved in the peer-review or handling of the manuscript. The authors have no competing interests to declare that are relevant to the content of this article.

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