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Aged Biochar–Nanoparticle Composites for Agricultural Soil Remediation: Mechanistic Insights, Engineering Design, Ecological Risks, and Translational Perspectives

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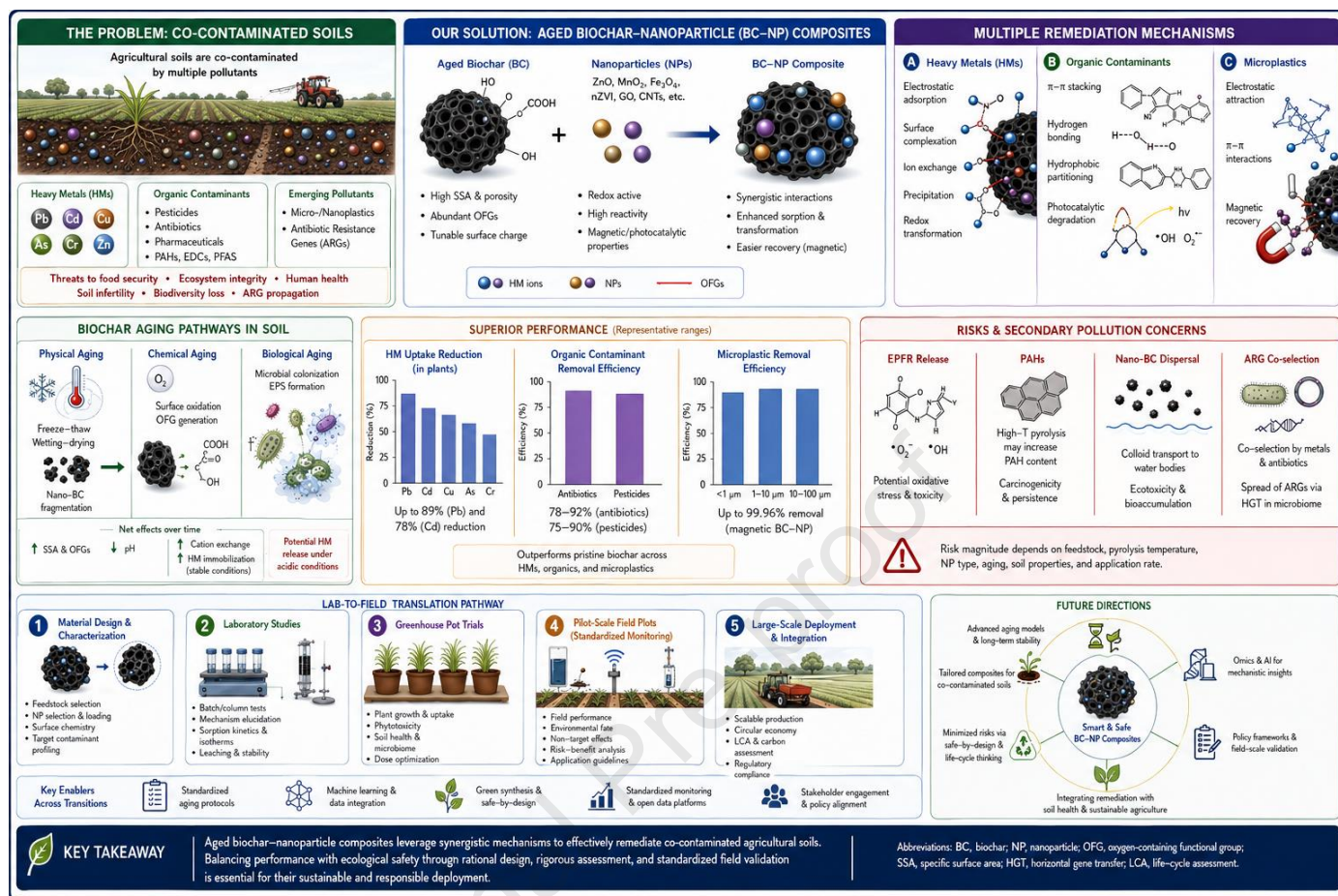
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Abstract

Agricultural soils increasingly receive mixtures of toxic metals, pesticides, antibiotics, and micro- and nanoplastics, creating simultaneous risks to crop productivity, food safety, soil biological function, and water quality. Biochar is a scalable carbonaceous amendment, but its performance evolves after application because oxidation, fragmentation, mineral association, and microbial colonization alter the reactive interface. This review advances an aging–engineering–risk–translation framework that links time-dependent biochar transformation with nanoparticle functionalization and field performance, rather than treating fresh biochar or nanocomposites as static adsorbents. The literature was critically screened with emphasis on 2019–2026 studies and earlier mechanistic papers where required. Natural aging can increase oxygen-containing surface functionality and organo-mineral association, and multi-year field evidence shows that immobilization of lead, copper, and cadmium can strengthen with aging under favorable conditions. Nanoparticle-modified biochars add contaminant-specific functions, including ligand exchange, redox transformation, photocatalytic oxidation, and magnetic recovery; however, the optimum design is soil- and contaminant-specific rather than universally transferable. The review also evaluates secondary risks, including nanoparticle detachment or dissolution, environmentally persistent free radicals, polycyclic aromatic hydrocarbons, mobile nano-biochar, antibiotic resistance determinants, and effects on microorganisms, soil enzymes, earthworms, and plants. A central conclusion is that high removal percentage alone is an inadequate endpoint: durable immobilization, transformation-product toxicity, biological function, recoverability, lifecycle burden, and field aging must be evaluated together. These insights provide a mechanistic basis for designing safer, durable, and field-relevant biochar–nanoparticle systems for agricultural soil remediation.

Keywords: Agricultural Pollution; Aged Biochar; Biochar Environmental Engineering; Heavy Metals; Nanoparticles; Oxygen-Containing Functional Groups; Soil Remediation

Graphical Abstract



Graphical Abstract. The conceptual synthesis of the aging–engineering–risk–translation framework. The scheme links physical, chemical, and biological aging with nanoparticle-enabled adsorption, complexation, redox transformation, photocatalysis, and magnetic recovery, while explicitly identifying secondary-pollution pathways and field-translation requirements.

1. Introduction

Agricultural soil contamination increasingly involves mixtures rather than single pollutants. Toxic metals, pesticide residues, veterinary and human pharmaceuticals, plastic-derived particles, and other contaminants of emerging concern can coexist with variable soil pH, organic matter, mineralogy, redox status, and microbial activity. This complexity is important because pollutant speciation and competition determine mobility, bioavailability, and the effectiveness of in situ amendments [1–6].

For toxic metals, remediation also depends on reliable measurement at environmentally relevant concentrations. Conventional instrumental techniques, such as inductively coupled plasma mass spectrometry, inductively coupled plasma optical emission spectrometry, and atomic absorption spectroscopy, remain central to confirmatory analysis, but electrochemical approaches can provide simpler, low-cost screening. For example, clinoptilolite-nanoparticle-modified carbon-paste electrodes have been developed for the sensitive voltammetric determination of Sn(II) and Hg(II), demonstrating how ion exchange, ligand enrichment, and electrochemical preconcentration can be combined for trace-metal sensing [7,8]. These analytical tools complement, rather than replace, laboratory reference methods and support rapid monitoring of remediation performance.

Conventional remediation technologies, including excavation, soil washing, thermal treatment, and electrokinetic processes, can be effective but are often costly, disruptive, or difficult to deploy across large agricultural areas. Biochar offers an alternative platform because it can be produced from agricultural residues and engineered through feedstock selection, pyrolysis conditions, mineral enrichment, oxidation, and nanoparticle functionalization. Its porous carbon matrix, mineral phases, aromatic domains, and oxygen-containing surface groups support electrostatic interactions, ion exchange, complexation, precipitation, hydrophobic partitioning, and π - π interactions [1,2,9]. However, biochar is not a static adsorbent once incorporated into soil. Temperature fluctuations, wetting-drying and freeze-thaw cycles, oxygen exposure, root activity, dissolved organic matter, soil minerals, and microbial colonization drive progressive fragmentation, oxidation, and surface coating. These aging processes may strengthen or weaken contaminant retention, depending on soil chemistry and the dominant binding mechanism [1,2,10-13].

A second limitation is that pristine biochar is rarely optimal for all contaminants. Biochar-nanoparticle (BC-NP) composites can add catalytic, redox, magnetic, or selective sorption functions. Metal oxides such as MnO_2 , ZnO , Fe_2O_3 , and Fe_3O_4 , nano zero-valent iron, and carbonaceous or semiconductor phases can broaden the range of target contaminants and accelerate transformation kinetics. Yet nanoparticle addition also raises new questions about dissolution, detachment, ecotoxicity, recoverability, and long-term transformation during aging.

This review's novelty therefore does not stem merely from extending the publication window. Earlier reviews have addressed biochar aging, biochar adsorption, modified biochars, or nanomaterials for environmental remediation separately. Here, these literatures are integrated around a specific engineering question: how should a BC-NP material be designed when its interface will continue to age in a biologically active, mineral-rich agricultural soil? The resulting aging-engineering-risk-translation framework explicitly links (i) time-dependent interfacial evolution, (ii) contaminant-specific composite design, (iii) ecological and secondary-pollution risks, and (iv) the evidence required for field translation.

This integration yields several cross-cutting insights. Aging should be treated as a design variable rather than solely as deterioration; the optimal composite is contaminant- and soil-specific; nanoparticle immobilization is as important as nanoparticle reactivity; the disappearance of a parent organic contaminant is not equivalent to detoxification; and remediation performance must be evaluated alongside soil biological function and long-term material fate. These points define the review's scientific and practical significance. Figure 1 presents the overview of the aging-engineering-risk-translation framework developed in this review.

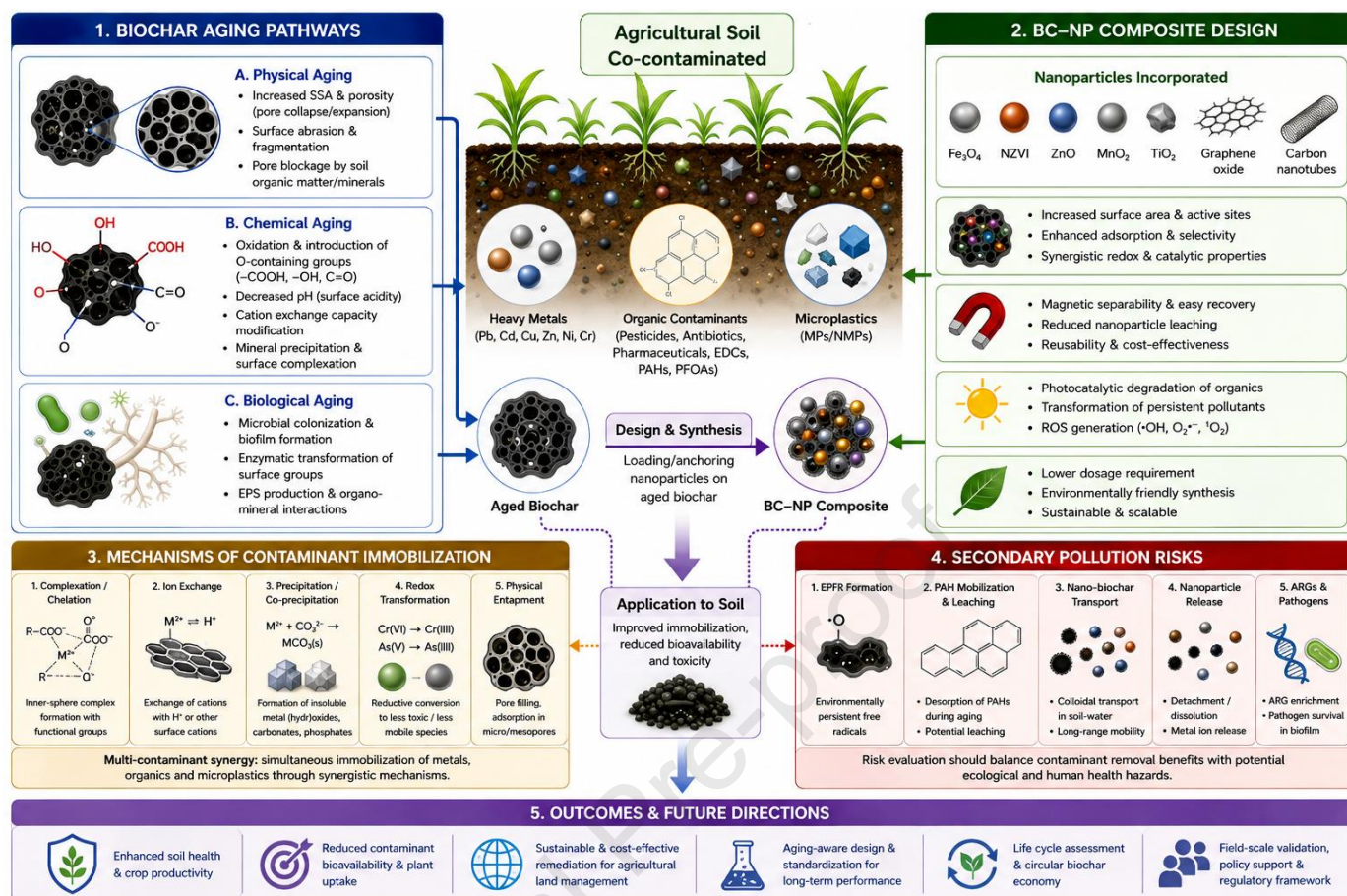


Figure 1. The overview of the aging-engineering-risk-translation framework developed in this review. Agricultural co-contaminants interact with fresh and aged biochar surfaces; nanoparticle functionalization adds selective adsorption, redox, photocatalytic, and magnetic functions; and long-term utility depends on the balance among contaminant immobilization/degradation, material aging, ecological safety, and field feasibility.

1.1 Literature search strategy and scope

A structured critical literature search was conducted using Web of Science, Scopus, PubMed, ScienceDirect, and Google Scholar as a supplementary discovery tool. Search strings combined “biochar” with “aging”, “aged biochar”, “nano-biochar”, “biochar nanoparticle composite”, “modified biochar”, “metal oxide biochar”, “magnetic biochar”, “nano zero-valent iron”, “agricultural soil”, “heavy metal”, “antibiotic”, “pesticide”, “microplastic”, “photocatalysis”, “environmentally persistent free radical”, “antibiotic resistance gene”, “ecotoxicity”, and “field remediation”. The core evidence window was 2019–2026; earlier studies were retained when they provided foundational mechanisms, analytical methods, natural-adsorbent comparisons, or field context. Priority was given to peer-reviewed studies reporting physicochemical characterization, contaminant speciation or bioavailability, mechanistic evidence, greenhouse/field validation, or ecotoxicological endpoints. Studies from aqueous systems were used only when their mechanistic relevance to composite design was explicit and were identified as such in the discussion. The present article is a critical narrative review rather than a formal systematic review or meta-analysis; therefore, no pooled effect size is claimed.

2. Biochar Aging in Agricultural Pedospheres

2.1 Physical, chemical, biological, and field aging

Physical aging encompasses mechanical abrasion, wetting–drying, freeze–thaw cycling, and photochemical exposure. Fragmentation can expose previously inaccessible surfaces and pores, but it can also generate colloidal and nanoscale biochar that is more mobile than the parent particles. Thus, the same process that increases the reactive surface area can create a carrier phase that facilitates contaminant transport through preferential flow paths [1,10,14].

Chemical aging is dominated by oxidation, leaching, and reactions with dissolved ions and mineral phases. Surface oxidation introduces carboxyl, phenolic, carbonyl, and related oxygen-containing groups and can alter the point of zero charge, cation exchange capacity, hydrophilicity, and metal-binding affinity. The magnitude and direction of these changes depend on feedstock, pyrolysis temperature, aging agent, and soil environment; they should not be generalized as universal fixed percentages [1,2, 15-17].

Biological aging involves microbial colonization, enzymatic transformation of labile carbon, extracellular polymeric substance formation, and interactions with roots and fungal hyphae. These processes can coat pores, alter sorption-site accessibility, and promote organo-mineral associations. Field aging integrates all of these processes and is therefore the most relevant but experimentally most difficult basis for predicting long-term performance [2,11,12]. Table 1 presents the major aging pathways and their implications.

Table 1. Major aging pathways and their implications. EPS, extracellular polymeric substances; ARG, antibiotic resistance gene. Changes are directional tendencies rather than universal responses because feedstock, pyrolysis conditions, soil pH, mineralogy, and aging duration strongly modify outcomes.

Aging pathway	Dominant drivers	Typical interfacial changes	Potential remediation benefit	Potential risk
Physical	Wetting–drying; freeze–thaw; abrasion; UV	Fragmentation; crack formation; altered pore accessibility	More exposed reactive surface	Mobile nano-biochar and contaminant co-transport
Chemical	O ₂ ; oxidants; acidic solutions; dissolved ions	Surface oxidation; mineral dissolution/neof ormation; altered charge	More ligand sites for cation complexation	Loss of alkaline buffering; desorption under acidification
Biological	Microbial colonization; enzymes; EPS; roots	Biofilm coating; labile-C loss; organo-mineral association	New binding environments; altered nutrient cycling	Surface fouling; uncertain ARG and microbiome effects
Natural field aging	Coupled abiotic and biotic forcing	Progressive oxidation plus mineral and organic coatings	Can strengthen long-term metal immobilization	Highly site-specific; difficult to accelerate reproducibly

2.2 Aging-dependent interfacial evolution and metal retention

A key finding from recent fieldwork is that aging does not necessarily cause a monotonic decline in performance. In a three-year field experiment, natural aging increased oxygen-containing groups and organo-mineral complexes on biochar, while the release risk of immobilized Pb, Cu, and Cd declined over time; co-precipitation and complexation were identified as major retention mechanisms [11]. Natural aging has likewise been reported to improve Pb immobilization and reduce phytotoxicity [12]. These observations support a shift from the simplistic “fresh versus degraded” view toward a mechanism-specific view in which aging changes the relative contributions of precipitation, ion exchange, and inner-sphere complexation. Simulated aging studies likewise show that aging can enhance stabilization of sorbed Cd and Pb, while oxidative treatment of nano-biochar can shift Cd retention toward more specific complexation mechanisms [15, 16]. Aging also alters nutrient-ion behavior: oxidation can increase ammonium adsorption while decreasing phosphate as surface charge and nitrogen-containing functionalities evolve [17].

The benefit is conditional. Acidification can protonate carboxylate and phenolate sites, dissolve mineral precipitates, and increase competition from H^+ and other cations. Thus, biochar that performs well in neutral soil may lose effectiveness in acid-mine-drainage-affected or strongly acidifying systems [13]. This pH dependence is central to predicting functional lifetime.

The concept of organo-mineral association also requires contaminant-specific interpretation. For mercury, Hg(II) denotes inorganic mercury in the +2 oxidation state and should not be equated with organomercury. Inorganic Hg(II) can complex with oxygen- and sulfur-containing ligands and associate with Fe/Mn phases, whereas organomercury species, such as methylmercury, arise through distinct transformation pathways. Because mobility and toxicity differ, mercury monitoring should distinguish inorganic Hg(II), dissolved complexes, and methylated forms where relevant.

2.3 Reactive oxygen species, EPFRs, and aging-derived organics

Environmentally persistent free radicals (EPFRs) can be stabilized by condensed aromatic structures and transition-metal centers. Their reaction with oxygen and water may generate reactive oxygen species (ROS), including superoxide and hydroxyl radicals. ROS reactivity is pH-dependent because proton-coupled redox potentials, semiconductor band-edge positions, surface charge, and radical lifetimes vary with solution chemistry. Hydroxyl radicals are highly reactive and relatively nonselective, whereas superoxide and photogenerated holes can show distinct substrate preferences. Recent analysis of biochar-derived EPFRs further emphasizes that radical abundance and persistence depend on feedstock chemistry, pyrolysis conditions, redox-active minerals, and environmental aging, making EPR characterization and ROS assays important components of safety assessment [18].

ROS may oxidize phenolic compounds and other hazardous organics associated with biochar aging via hydroxylation, electron transfer, bond cleavage, and ring opening. However, transformation does not necessarily mean detoxification. Partial oxidation can produce mobile or biologically active intermediates. Scavenger experiments, chromatographic and mass-spectrometric product identification, mineralization measurements, and toxicity assays are therefore required to distinguish beneficial degradation from incomplete transformation. Figure 2 presents the conceptual diagram of biochar aging in agricultural soil.

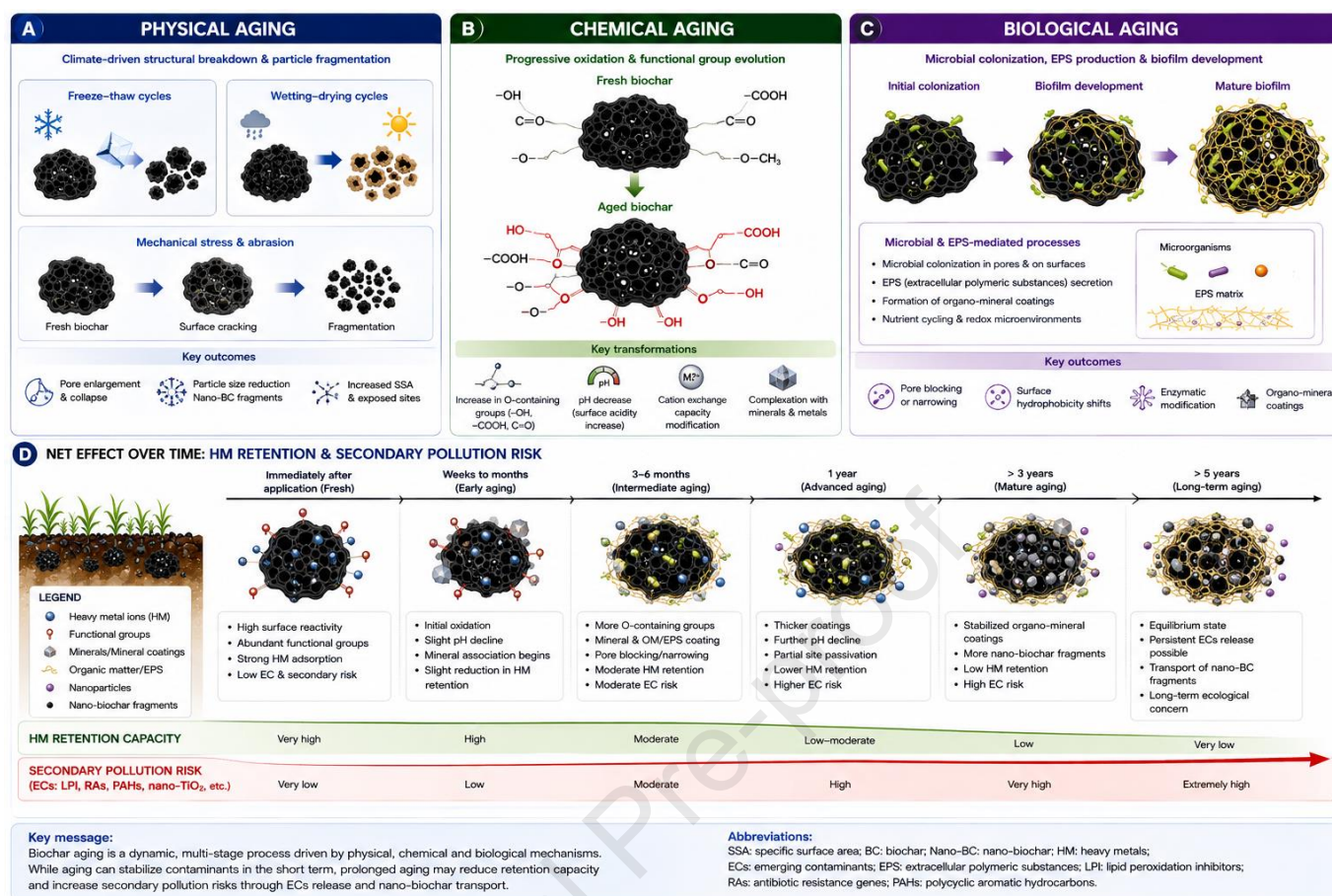


Figure 2. The conceptual diagram of biochar aging in agricultural soil: (A) physical fragmentation under wetting–drying and freeze–thaw cycles; (B) chemical oxidation and development of oxygen-containing functional groups; (C) biological colonization, extracellular polymeric substances, and organo-mineral coatings; and (D) time-dependent consequences for contaminant retention, colloidal mobility, and secondary-pollution risk. BC, biochar; EPS, extracellular polymeric substances.

3. Engineering BC–NP Composites

3.1 Functional architecture and contaminant specificity

Composite engineering aims to couple biochar's broad sorption capacity with a second phase that provides a defined function. MnO₂ contributes highly reactive hydroxylated surfaces and redox chemistry; ZnO provides amphoteric sorption sites and semiconductor photocatalysis; Fe₃O₄ adds iron-oxide binding sites and magnetic responsiveness; nano zero-valent iron enables reductive transformation; and graphitic carbon nitride (g-C₃N₄) provides visible-light-responsive semiconductor behavior. The biochar scaffold can reduce nanoparticle aggregation, concentrate contaminants near reactive phases, and facilitate electron transfer, but excessive loading may block pores or increase ecological exposure. Table 2 presents comparative engineering features of BC–NP synthesis routes.

Metal oxides should not be described as acting through a single generic “ion-exchange/photodegradation” mechanism. Their roles depend on surface hydroxylation, point of zero charge, band structure, oxidation state, and the biochar–oxide interface. ZnO is primarily a semiconductor and an amphoteric sorbent; Fe oxides support complexation, redox and Fenton-like reactions, and, for Fe₃O₄, magnetic recovery; MnO₂ provides strong surface complexation and oxidative reactivity.

3.2 In situ versus ex situ synthesis and secondary-pollution control

Table 2. Comparative engineering features of BC–NP synthesis routes. NP, nanoparticle; BC–NP, biochar–nanoparticle composite. The “best” route depends on the target contaminant, required stability, intended recovery strategy, and field application mode.

Route	Advantages	Disadvantages	Secondary-pollution control priority
In situ formation	Strong NP anchoring; intimate interface; reduced aggregation; often lower detachment	Less independent control of NP size/phase; precursor may alter pyrolysis; pore blockage possible	Optimize precursor dose; wash residual salts; leaching/aging tests
Ex situ deposition	Independent optimization of biochar and NP; flexible loading; easier phase selection	More processing; aggregation/detachment risk; solvent/reagent demand	Covalent/ligand anchoring; pore confinement; recovery tests
Green/biogenic synthesis	Reduced use of harsh reducing agents; potential use of biomass extracts	Composition can be variable; scale-up reproducibility may be difficult	Standardize extract chemistry and residual organics
Magnetic design	Enables recovery in water/slurry systems	Recovery is difficult in intact field soil; Fe loading can alter pH/redox	Use only where recoverability is realistic; verify Fe release

Strategies to reduce secondary pollution include in situ nanoparticle growth, pore-confined synthesis, ligand or covalent anchoring, using earth-abundant Fe-based phases where appropriate, optimizing rather than maximizing nanoparticle loading, prewashing to remove soluble synthesis residues, and predeployment leaching/aging tests across relevant pH and ionic-strength ranges. Magnetic recovery is useful in water, slurry, or ex situ soil-washing systems but should not be presented as universally feasible in intact field soils. Acid- and alkali-modification studies further show that surface activation can markedly alter pore accessibility and oxygen-containing functionality, but aggressive chemical activation can increase reagent use and washing requirements [19]. Plant-mediated synthesis of metal nanoparticles offers a complementary, lower-chemical-intensity route and may reduce reliance on hazardous reducing agents, although reproducibility, extract composition, and nanoparticle standardization remain important scale-up challenges [20]. Figure 3 presents the mechanistic framework for BC–NP composite remediation.

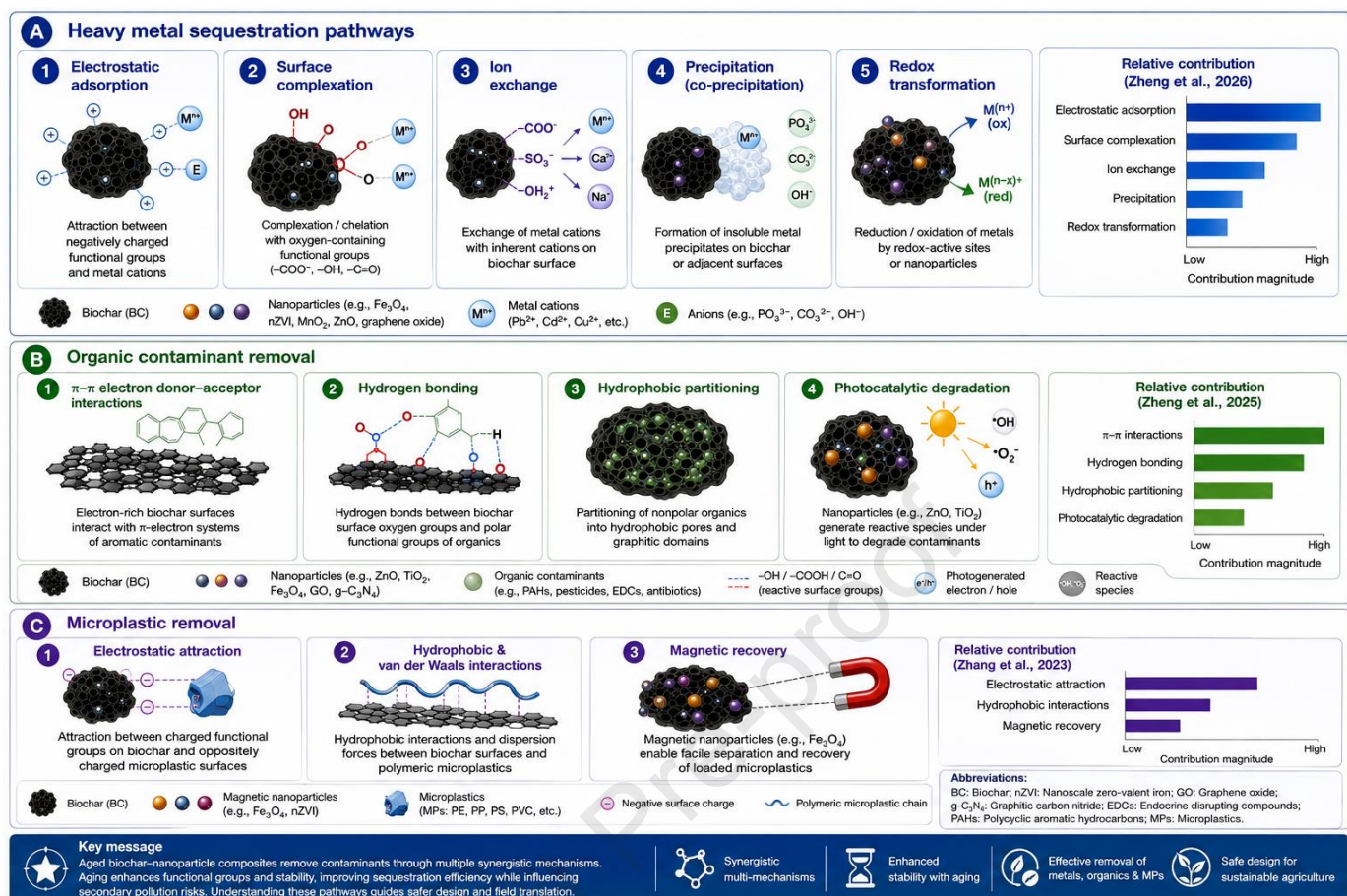


Figure 3. Mechanistic framework for BC–NP composite remediation. (A) Cationic metals: electrostatic attraction, ion exchange, inner-sphere complexation, and mineral precipitation; (B) Cr(VI) and other redox-sensitive species: anion-responsive surfaces and reductive transformation; (C) organic contaminants: pore filling, hydrophobic partitioning, π – π interactions, and ROS-mediated photocatalysis; and (D) microplastics: adsorption/heteroaggregation followed by magnetic recovery. BC–NP, biochar–nanoparticle composite; ROS, reactive oxygen species.

3.3 Adsorption, ion exchange, complexation, precipitation, and redox transformation

For cationic metals such as Pb^{2+} and Cd^{2+} , BC–NP composites may involve electrostatic attraction, ion exchange, inner-sphere complexation, and precipitation. These mechanisms should be distinguished. Ion exchange involves replacing exchangeable cations; electrostatic attraction is non-specific and charge-dependent; inner-sphere complexation involves direct coordination to surface ligands; and precipitation produces a new solid phase.

Natural zeolites provide a useful mechanistic comparison. Clinoptilolite possesses permanent negative framework charge balanced by exchangeable cations, whereas biochar exchange capacity is more heterogeneous and arises from deprotonated surface groups and mineral-associated sites. Functionalizing clinoptilolite with EDTA, glutamic acid, DTPA, or cysteine shows how ligand complexation can act synergistically with ion exchange for $\text{Pb}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Cd}(\text{II})$, and $\text{Cu}(\text{II})$ removal [21–24]. Biochar offers less crystallographically uniform exchange sites but greater tunability, aromatic domains for organic sorption, redox-active phases, and a carbon-sequestration co-benefit.

Cr(VI) requires a different design logic because it occurs primarily as oxyanions such as HCrO_4^- , CrO_4^{2-} , and $\text{Cr}_2\text{O}_7^{2-}$, depending on pH and concentration. Negatively charged biochar surfaces may repel these species.

Effective strategies include protonated/positively charged sites, anion-exchange functionality, Fe-containing phases, and, especially, reduction of Cr(VI) to Cr(III) followed by complexation or precipitation. Surfactant-modified clinoptilolite provides a mechanistic example of converting a cation exchanger into an anion-responsive surface for dichromate sensing [25].

3.4 Comparison with other natural and bio-based adsorbents

Biochar should be evaluated alongside other low-cost sorbents rather than in isolation. Zeolites offer defined ion-exchange sites and mineral stability; cellulose- and chitosan-based sorbents offer renewable hydroxyl or amino functionality and can be magnetized or ligand-functionalized; silica-based sorbents provide controllable surface chemistry. Biochar's comparative strengths include feedstock circularity, mixed inorganic/organic sorption, tunable mineral content, compatibility with soil incorporation, and carbon storage. Its limitations include heterogeneity, possible PAH/EPFR formation, aging-dependent behavior, and often lower selectivity without functionalization. This comparison supports hybrid designs when selectivity, biodegradability, catalytic function, or recoverability is a priority. Nutrient-sorption studies with cacao-shell and corn-cob biochars also demonstrate that feedstock mineralogy and surface chemistry strongly influence phosphate and ammonium retention, reinforcing the need to select feedstocks for the intended remediation chemistry rather than treating all biochars as equivalent [26].

4. Contaminant-Specific Remediation Performance and Mechanisms

4.1 Heavy metals and metalloids

In a greenhouse study of multi-metal-contaminated soil under ryegrass, biochar modified with MnO₂ or ZnO nanoparticles reduced plant uptake more than pristine biochar. At 0.5–1% application, MnO₂-modified biochar reduced shoot Pb uptake by 83.82–89.33% and Cd uptake by 78.73–82.83% relative to the control; ZnO-modified biochar also strongly reduced Pb and Cd uptake but increased Zn uptake, illustrating that a composite can immobilize one target while increasing exposure to an element contained in the modifier itself [27]. This result cautions against ranking materials solely by a single removal endpoint.

The underlying interactions include deprotonated carboxyl/phenolic groups on biochar, hydroxylated Mn–O or Zn–O surface sites, ion exchange with Ca²⁺/Mg²⁺/K⁺, and precipitation as carbonate, phosphate, or hydroxide where local chemistry permits. Conceptually, $\equiv\text{BC}-\text{COO}^- + \text{Pb}^{2+}$ can form $\equiv\text{BC}-\text{COO}-\text{Pb}^+$, while $\equiv\text{Mn}-\text{OH}$ sites can form inner-sphere Mn–O–Pb complexes with proton release. The relative contribution of each pathway varies with pH, competing ions, mineral phases, and aging.

Field evidence remains more limited than batch and greenhouse evidence. The three-year study of naturally aged biochar provides particularly important support for the progressive stabilization of Pb, Cu, and Cd [11], and natural aging has also improved Pb immobilization and reduced phytotoxicity [12]. These studies justify long-term evaluation of BC–NP composites themselves, because nanoparticle phases may transform even as the underlying biochar becomes more oxidized and mineral-associated. Additional evidence shows that urban-green-waste biochar can reduce Cd bioavailability, supporting the broader principle that feedstock-derived mineral phases and surface functionality can be exploited for Cd stabilization [28]. Figure 4 presents the contaminant-specific performance framework for BC–NP composites.

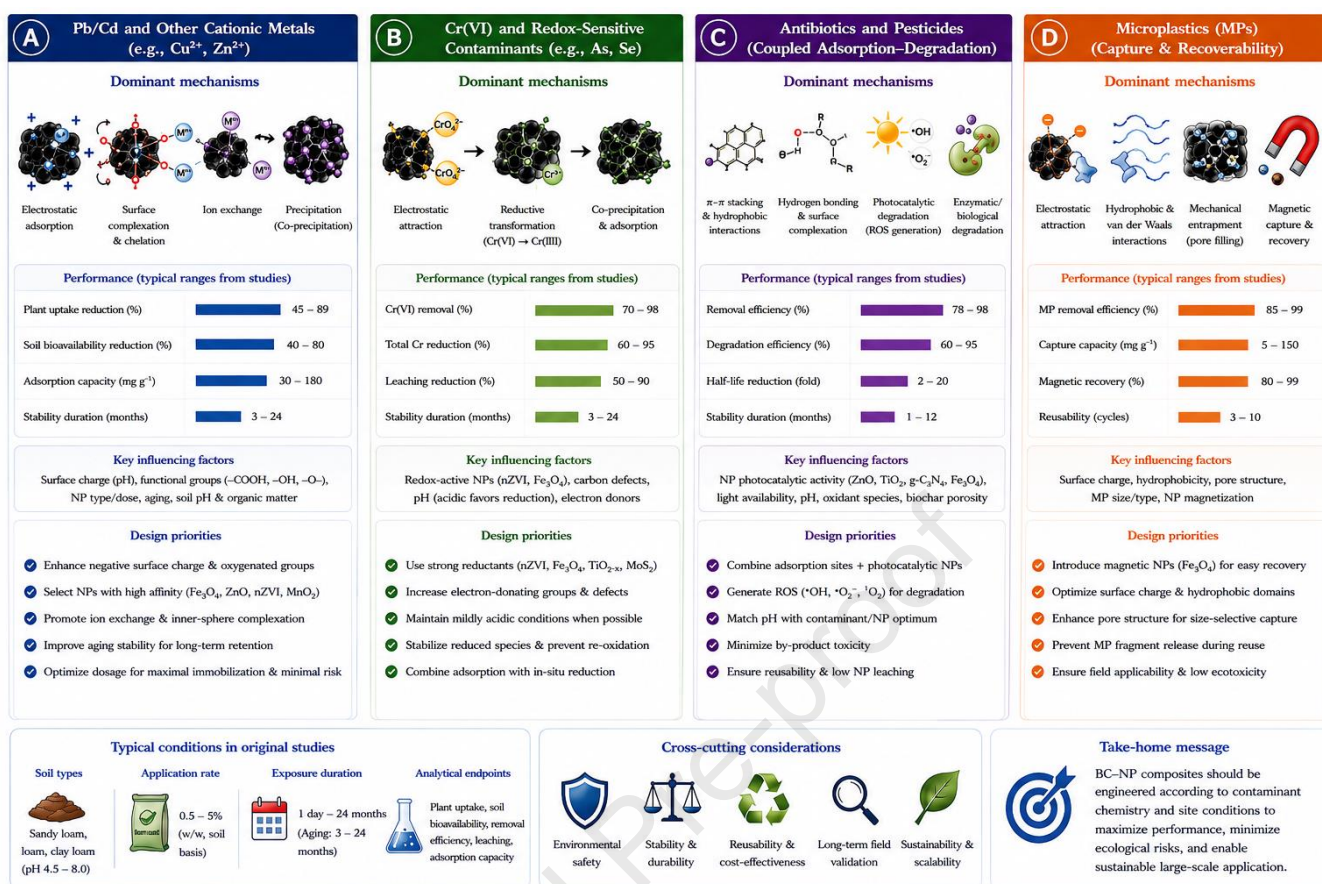


Figure 4. Contaminant-specific performance framework for BC–NP composites. Panels compare the dominant design requirements for (A) Pb/Cd and other cationic metals, (B) Cr(VI) and redox-sensitive contaminants, (C) antibiotics and pesticides requiring coupled adsorption–degradation, and (D) microplastics requiring capture and recoverability. Interpret values reported in the text within the soil type, application rate, exposure duration, and analytical endpoint of the original studies.

4.2 Antibiotics, pesticides, and other xenobiotic organics

For aromatic organic contaminants, biochar contributes π – π electron donor–acceptor interactions, hydrophobic partitioning, hydrogen bonding, and pore filling. Semiconductor phases add destructive transformation. A mechanistically complete photocatalytic sequence includes: (1) adsorption/diffusion of the contaminant to the interface; (2) photon absorption; (3) generation of conduction-band electrons and valence-band holes; (4) charge separation and interfacial transfer; (5) formation of ROS; (6) oxidation/reduction of the parent molecule; (7) formation of intermediates; and, where sufficient oxidative capacity is sustained, (8) mineralization.

The basic reactions can be represented as $\text{Semiconductor} + h\nu \rightarrow e^-(\text{CB}) + h^+(\text{VB})$; $\text{O}_2 + e^- \rightarrow \text{O}_2^{\cdot-}$; and $\text{H}_2\text{O}/\text{OH}^- + h^+ \rightarrow \cdot\text{OH}$. Heterojunctions, plasmonic metals, and conductive carbon supports can suppress electron–hole recombination and extend light harvesting. In a double plasmonic $\text{Ag}@\text{AgCl}/\text{Cu}@\text{Cu}_2\text{O}$ system, scavenger experiments identified superoxide and hydroxyl radicals as the major reactive species, and LC–MS was used to identify tetracycline transformation products [29]. This evidence illustrates why the disappearance of the parent compound should not be equated with detoxification.

For BC–NP systems, the engineering implication is to deliberately couple adsorption and catalysis: adsorption concentrates the contaminant near the catalytic interface, while the semiconductor or redox phase transforms it. However, strong adsorption can also shield molecules from light or reactive species, and natural organic

matter can compete for radicals. Therefore, catalyst loading, optical accessibility, pore architecture, and soil moisture must be optimized together, not independently.

4.3 g-C₃N₄ and heterojunction photocatalysts

Graphitic carbon nitride (g-C₃N₄) is attractive because it is metal-free, visible-light responsive, chemically stable, and can be produced from inexpensive nitrogen-rich precursors. Bulk g-C₃N₄, however, suffers from limited surface area and rapid electron-hole recombination. Nanosheet formation, defect engineering, heterojunction construction, coupling with conductive carbon, and Z-scheme or step-scheme architectures can improve charge separation while preserving strongly reducing electrons and strongly oxidizing holes. Carbon or nitrogen vacancies can further modify the band structure and adsorption sites. For agricultural remediation, these gains must be balanced against limitations on light penetration in soil and the need to identify transformation products rather than relying solely on removal percentages.

4.4 Microplastic and nanoplastic interception and magnetic recovery

Magnetic species do not generally “degrade” microplastics. Instead, carbonaceous and mineral surfaces capture plastic particles, after which Fe₃O₄ or another magnetic phase can render the contaminant-loaded aggregate responsive to an external field. Capture may involve hydrophobic interactions, van der Waals forces, π - π interactions for aromatic polymers such as polystyrene, hydrogen bonding to oxygenated or weathered plastic surfaces, electrostatic attraction, cation bridging, and physical interception. Weathering can introduce carbonyl and carboxyl groups that alter these interactions.

The practical sequence is therefore microplastic adsorption/heteroaggregation → formation of a BC-Fe₃O₄-plastic aggregate → magnetic separation and recovery. This approach is most applicable in water, slurry, drainage, or ex situ soil-washing systems. Reported near-complete removal in controlled matrices should not be extrapolated directly to intact agricultural soils, where magnetic retrieval, particle heterogeneity, mineral interference, and root/aggregate structure complicate recovery. This caution matters because micro- and nanoplastics can be taken up by plants and affect root development, oxidative balance, and physiological function; remediation therefore requires both capture efficiency and verification that treatment does not create a more mobile particle fraction [30]. Table 3 emphasizes that a composite optimized for one contaminant class may not be optimal or even benign for another.

Table 3. Contaminant-specific design logic for BC-NP composites. BC, biochar; ROS, reactive oxygen species.

Target	Preferred composite function	Dominant mechanisms	Key design caveat
Pb ²⁺ , Cd ²⁺	MnO ₂ /Fe oxide/mineral-rich BC	Complexation; ion exchange; precipitation	Acidification can weaken retention
Cr(VI)	Fe-bearing/reductive or positively functionalized BC	Anion attraction/exchange; reduction to Cr(III); precipitation	Speciation is pH dependent
Antibiotics/pesticides	Aromatic BC + semiconductor/heterojunction	π - π sorption; H-bonding; ROS oxidation	Transformation products and mineralization must be measured
Microplastics	Magnetic, hydrophobic/aromatic BC	Heteroaggregation; hydrophobic/ π interactions; magnetic recovery	Field-soil recovery is difficult
Mixed contamination	Multifunctional composite	Competitive sorption + redox/catalysis	One modifier may introduce a new ion or toxicity

5. Ecological and Biological Risk Assessment

5.1 Soil microorganisms, beneficial microbiota, and antibiotic resistance

Biochar can create porous refugia, adsorb inhibitory contaminants, modify pH, and supply mineral nutrients, thereby altering microbial biomass and community composition. Aging further alters these microhabitats through oxidation, mineral coating, and extracellular polymeric substances. The direction of response depends on context: improved habitat and reduced contaminant bioavailability can support microbial function, whereas nanoparticle dissolution, EPFR-derived oxidative stress, or excessive alkalinity can suppress sensitive taxa.

Beneficial rhizosphere organisms deserve explicit attention. Plant-growth-promoting bacteria, mycorrhizal fungi, and other mutualists contribute to nutrient acquisition and stress tolerance; a remediation material that immobilizes metals but disrupts these functions may not confer a net ecological benefit. Antibiotic-contaminated soils add another layer because biochar can reduce freely dissolved antibiotic concentrations while also providing surfaces for dense biofilms. The net effect on antibiotic resistance genes depends on contaminant loading, feedstock, aging state, and microbial community structure and should be measured rather than assumed.

5.2 Soil enzymes and functional endpoints

Soil enzymes integrate microbial activity and nutrient cycling and serve as useful early-warning endpoints. Dehydrogenase reflects overall microbial oxidative activity; urease participates in nitrogen cycling; phosphatases regulate mineralization of organic phosphorus; β -glucosidase reflects carbon cycling; and catalase responds to oxidative conditions. Biochar may increase enzyme activities by improving habitat and reducing contaminant bioavailability, but high nanoparticle doses or ROS-generating phases can suppress activity. Future BC–NP studies should therefore pair chemical immobilization metrics with a minimum biological panel that includes microbial diversity and function, along with representative C-, N-, and P-cycling enzymes.

5.3 Earthworms, plants, and trophic exposure

Earthworms are directly exposed via dermal contact and ingestion and can alter particle size, surface coatings, and microbial associations during gut passage. Relevant endpoints include survival, biomass, reproduction, oxidative-stress biomarkers, tissue metal accumulation, and changes in the gut microbiome. Plant assessment should likewise extend beyond biomass to root architecture, photosynthetic performance, nutrient balance, oxidative stress, and contaminant concentrations in edible tissues. These endpoints are essential for determining whether chemical immobilization translates into ecological recovery and food-safety benefits. Graphene oxide provides a relevant example of why modifier-specific phytotoxicity must be considered: exposure has been associated with pH alteration, iron overload, and oxidative damage in rice, indicating that enhanced sorption performance cannot be evaluated independently of plant nutrient homeostasis and redox stress [31].

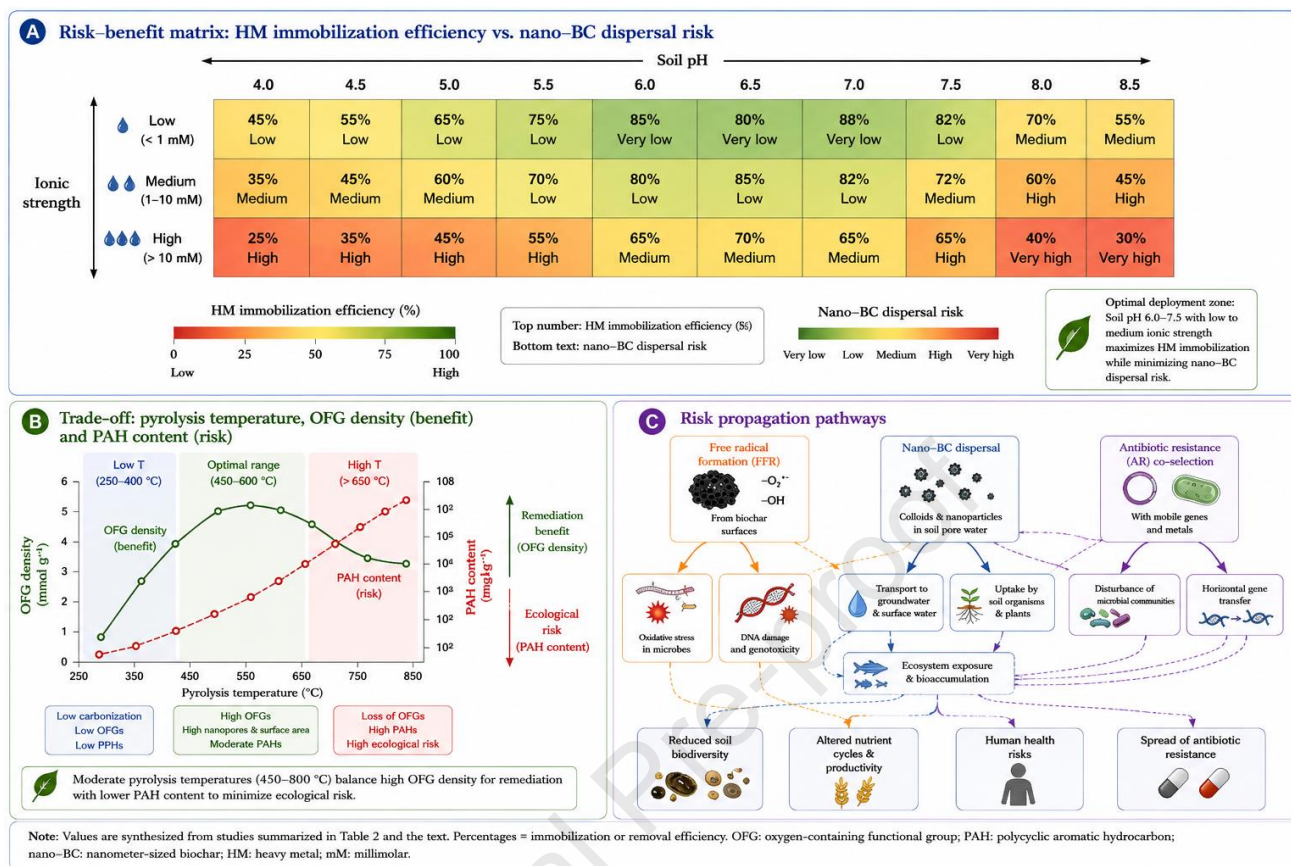


Figure 5. Risk–benefit framework for aged BC–NP composites. The scheme integrates remediation benefit with potential nanoparticle dissolution/detachment, nano-biochar mobility, environmentally persistent free radicals, polycyclic aromatic hydrocarbons, antibiotic-resistance dynamics, soil-enzyme responses, beneficial microorganisms, earthworms, plant uptake, and food-chain exposure. EPFR, environmentally persistent free radical; ARG, antibiotic resistance gene.

5.4 Nanoparticle fate, EPFRs, PAHs, and nano-biochar mobility

Nanoparticle fate is governed by dissolution, aggregation, redox transformations, sulfidation or mineral conversion, and the formation of natural-organic-matter coronas. ZnO is particularly sensitive to acid dissolution, creating a potential Zn^{2+} exposure pathway; graphene-based materials may alter rhizosphere chemistry and oxidative balance. EPFRs and PAHs add intrinsic risks to some biochars, while physical aging can generate mobile nano-biochar. These processes argue for an exposure-based assessment that measures what is released or bioavailable over time, not only the nominal nanoparticle loading in the original material. Table 4 lists EPR (electron paramagnetic resonance), DOC (dissolved organic carbon), ARG (antibiotic resistance gene), and qPCR (quantitative polymerase chain reaction).

Table 4. Minimum risk endpoints for field-oriented evaluation of aged BC–NP composites.

Risk endpoint	Mechanistic origin	Recommended measurement	Decision relevance
NP release/dissolution	Weak anchoring; acidic dissolution; aging	Leachate metal/particle analysis; aging tests	Secondary exposure and material durability
EPFR/ROS	Pyrogenic radicals; transition-metal centers	EPR; ROS probes; oxidative-stress biomarkers	Microbial/plant toxicity
PAH mobilization	Pyrolysis by-products; DOC-assisted desorption	Priority PAH analysis; pore-water concentration	Food-chain and soil-biota risk
Nano-biochar transport	Fragmentation and colloidal stabilization	Column transport; particle-size/zeta potential	Groundwater co-transport risk
Microbial function/ARGs	Biofilm habitat; antibiotic selection; NP stress	Metagenomics/qPCR; respiration; enzyme assays	Soil health and resistance dissemination
Earthworm/plant effects	Ingestion, root exposure, dissolved ions	Survival/reproduction; biomass; tissue burden	Ecological recovery and food safety

6. Bridging Laboratory Performance to Agricultural Field Use

The central translational problem is that most adsorption and photocatalysis studies oversimplify the soil environment. Batch tests often use high contaminant concentrations, well-mixed suspensions, short contact times, and single pollutants. Real soils impose diffusion limitations, competitive ions, dissolved organic matter, mineral coatings, wetting–drying cycles, plant uptake, microbial transformation, and spatial heterogeneity. Consequently, high Langmuir capacity or rapid aqueous degradation does not guarantee field performance.

A staged validation pathway is recommended: physicochemical design → batch mechanistic testing → column transport/leaching → greenhouse plant–soil trials → pilot field plots → multi-year field monitoring. At each stage, measure both efficacy and release/toxicity endpoints. Standardized accelerated-aging protocols are particularly important, but they should be calibrated against naturally aged field materials rather than assumed equivalent.

Conduct techno-economic and lifecycle analyses before scale-up. Nanoparticle synthesis energy, chemical reagents, washing water, feedstock transport, application equipment, potential recovery, and end-of-life management can offset environmental gains. The most sophisticated nanocomposite is not necessarily the most sustainable; an earth-abundant Fe/mineral modification that achieves adequate immobilization may outperform a high-cost multi-component photocatalyst when field conditions, lifecycle burden, and regulatory acceptance are considered. Green, plant-mediated nanoparticle synthesis may reduce some chemical inputs and improve circularity, but lifecycle and techno-economic analyses must confirm its benefits rather than assuming them from the term “green” alone [20]. The laboratory-to-field translation pathway for BC–NP composites is presented in Figure 6.

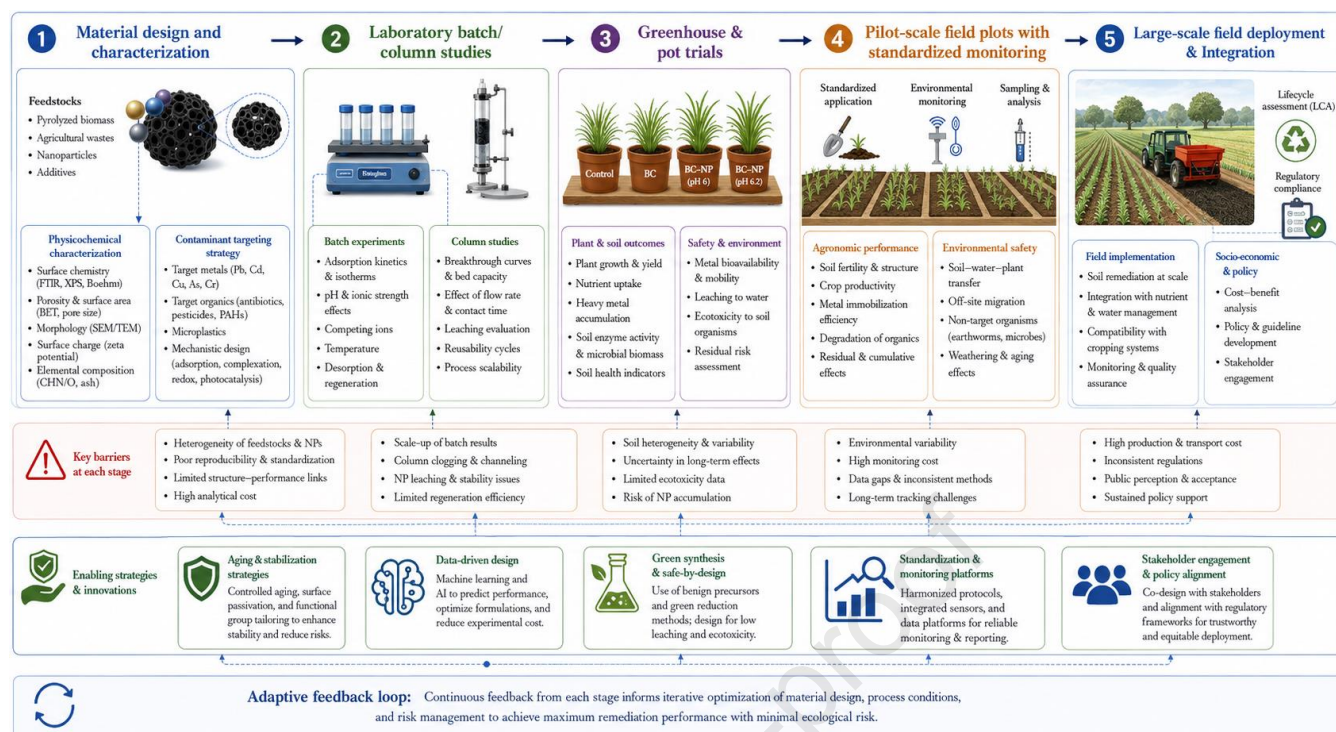


Figure 6. Laboratory-to-field translation pathway for BC–NP composites: (1) material design and physicochemical characterization; (2) batch mechanistic testing; (3) column transport and leaching; (4) greenhouse plant–soil trials; (5) pilot field plots; and (6) multi-year deployment coupled with lifecycle, techno-economic, ecological, and regulatory assessment. BC–NP, biochar–nanoparticle composite.

7. Limitations of the Current Evidence and This Review

The available evidence is heterogeneous across feedstock, pyrolysis temperature, nanoparticle phase and loading, soil type, contaminant concentration, aging protocol, exposure duration, and analytical endpoint. Direct quantitative comparison is therefore limited. Many studies use aqueous systems or artificially spiked soils, whereas naturally contaminated soils contain aged contaminant pools and complex mineral/organic associations. Long-term field studies of BC–NP composites are scarce, and data on PFAS, micro- and nanoplastics, transformation products, antibiotic resistance determinants, and trophic transfer remain less mature than those for conventional metal cations. Ecotoxicological endpoints are also inconsistently reported. Finally, this is a structured critical narrative review, not a registered systematic review or meta-analysis; the conclusions therefore emphasize mechanistic convergence, contradictions, and research needs rather than pooled effect sizes.

8. Research Gaps and Future Engineering Perspectives

First, long-term, multi-site field trials should track both the carbon scaffold and the nanoparticle phase. Surface spectroscopy, sequential extraction/speciation, particle tracking, pore-water chemistry, plant uptake, and biological endpoints should be measured repeatedly to link material transformation causally to performance.

Second, accelerated aging should be predictive, not merely comparative. Wetting–drying, freeze–thaw, oxidation, acidification, mineral coating, and biological colonization need to be calibrated against field-aged reference materials. The objective is not to reproduce every field process but to predict a bounded performance envelope under defined pedoclimatic conditions.

Third, composite design should shift from “maximum loading” to “minimum effective functionality”. Machine learning and inverse design can identify combinations of feedstock, pyrolysis temperature, surface functionality, mineral phase, and nanoparticle loading that achieve a target risk reduction while minimizing material and lifecycle burden. Training datasets must include negative outcomes and release/toxicity data, not only adsorption capacity. Recent machine-learning work using experimental biochar–metal datasets demonstrates the potential to rank soil and material descriptors and predict adsorption/remediation outcomes [32]. Earlier predictive work also showed that feedstock C/N ratio and pyrolysis temperature can explain Cu and Zn sorption capacity, providing a foundation for data-guided material selection [33].

Fourth, remediation endpoints should be multidimensional. For metals, this includes speciation, leachability, plant uptake, and stability under acidification. For organics, this includes parent loss, transformation products, mineralization, and toxicity. For microplastics, this includes capture and realistic recovery. Across all classes, incorporate soil enzymes, beneficial microorganisms, earthworms, crop performance, and food-chain transfer.

Finally, regulatory frameworks should distinguish between freely applied nanoparticles and those strongly immobilized within a carbon/mineral matrix, while still requiring evidence of release during aging. Product specifications should include feedstock provenance, pyrolysis conditions, contaminant limits, nanoparticle composition/loading, leachable fraction, particle release, and standardized ecotoxicity tests. These criteria would link materials innovation to responsible agricultural deployment.

9. Conclusions

Aged BC–NP composites are best understood as evolving reactive interfaces rather than as fixed adsorbents. Aging can increase oxygen-containing functional groups and organo-mineral associations and, under suitable conditions, strengthen long-term metal immobilization. Nanoparticle functionalization can add redox, photocatalytic, selective sorption, and magnetic functions, but the benefit is contaminant- and soil-specific and must be weighed against dissolution, detachment, ROS/EPFR generation, and biological effects.

This review's main contribution is integrating aging, engineering, ecological risk, and field translation into a single decision framework. This synthesis shows that short-term removal efficiency alone is insufficient and that a successful material must retain contaminants under realistic aging, avoid unacceptable secondary exposure, preserve soil biological function, and remain economically and operationally feasible.

Accordingly, the most promising path is not indiscriminate against nano-functionalization but the rational design of the simplest composite that delivers the required mechanism, remains stably anchored during aging, and demonstrates net benefit across contaminants, crops, soil biology, lifecycle, and regulatory endpoints. This aging-aware design principle offers a clearer path from laboratory innovation to safe agricultural remediation.

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Highlights

- Aging universally increases OFG density and SSA while reducing pH, with chemical aging having the greatest quantitative impact on sorption capacity.
- Three years of field evidence demonstrate that natural aging can progressively enhance HM immobilization through organo-mineral complexation, challenging assumptions about performance decline.
- BC–NP composites (ZnO, MnO₂, Fe₃O₄, nZVI, GO, CNTs) reduce phytoavailability of Pb and Cd by up to 89% and 78%, respectively, through synergistic, multi-mechanism sequestration.
- Magnetized BC composites achieve nearly complete microplastic removal (99.96%), independent of particle size, with magnetic sorbent recovery enabling circularity.
- Secondary risks, including EPFRs, PAH mobilization, nano-BC dispersal, ARG co-selection, and NP ecotoxicology, require lifecycle-integrated assessment frameworks for safe deployment.

Declaration of Competing Interest

The author declares that he has no known competing financial interests or personal relationships that could have influenced the work reported in this paper.