



Biogenic nanoparticles in the “plant – microbiome – soil” system: Biological synthesis platforms and regulatory interactions

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The plant – microbiome – soil system is an environment in which biogenic nanoparticles are formed and simultaneously act as regulatory factors: biological platforms of different taxonomic origin govern precursor conversion, while the resulting particles alter plant physiology, the structure of rhizosphere multi-species communities and the chemical state of the soil. This narrative critical review compares bacteria, microalgae, endophytic fungi and plant extracts as platforms of particle formation and grades the strength of evidence for their action from the individual to the ecosystem level, with an emphasis on the agroecological context of contaminated soils. Publications retrieved from PubMed/MEDLINE, Web of Science, Scopus, ScienceDirect and Google Scholar, mainly for 2018–2026, were classified according to a four-level hierarchy: direct causal, strong functional, indirect and conceptual evidence. For elemental particles, enzymatic, thiol-mediated and polyphenol–flavonoid redox routes were distinguished; for metal oxides – hydrolysis, precipitation and biologically modulated mineralisation. Direct confirmation of a specific reductant is available only in individual systems, notably for fumarate reductase, whereas FTIR identification, pH shifts and correlations of enzyme activity remain indirect. Primary soil–plant studies show that biogenic FeO and Se nanoparticles can alter Cd availability, plant antioxidant responses and the recruitment of beneficial bacteria to the root zone; however, outcomes depend on dose, coating, size and soil matrix. Positive results have been obtained mainly in controlled aqueous, soil or pot systems; comparisons with soluble ions, non-nanoscale analogues and biological extracts are often incomplete, which limits causal inference. Ecotoxicological data indicate dose-dependent effects on soil invertebrates and microbial communities, which requires multi-species assessment. Engineered nanoscale zero-valent iron is considered separately as a model comparator of ageing, passivation and microbial reactivation, rather than as evidence for the properties of all biogenic particles. Field translation requires standardised characterisation, ionic and non-nanoscale controls, multi-species testing and long-term assessment of particle fate.

Keywords: rhizosphere microbiome; multi-species communities; redox mechanisms; ecobiotechnology; agroecology.

Introduction

The plant–microbiome–soil system is a multi-level biological entity in which roots, rhizosphere microbial communities and the mineral and organic phases of the soil are linked by flows of matter and signals. It is in this environment that living systems are able to convert metal ions into nanoscale elemental or oxide phases, while the resulting particles act on organisms at different levels of organisation – from the individual plant to the soil community as a whole. The applied significance of such conversions is greatest in the agroecological context: soils and aquatic systems contaminated with heavy metals, persistent organic compounds and synthetic dyes retain contaminants that are persistent and bioaccumulative, entering trophic chains through agricultural produce (Sharma et al., 2023; Z. Wang et al., 2024). Conventional physico-chemical remediation, including excavation, soil washing, chemical stabilisation and electrokinetic treatment, is constrained by cost, energy demand, generation of secondary waste and disruption of soil structure, whereas purely biological approaches are less destructive but may be slow, site-dependent and of limited efficiency under high contaminant loads (Badamasi et al., 2026; Chauhan et al., 2022).

Nanotechnology and biologically mediated, or “green”, synthesis of nanoparticles have been proposed as ways of extending the functional capacity of remediation systems (Alabrahim et al., 2025). In this context, nanoparticles have a dual biological status. First, they are products of living systems or biological extracts: bacteria, fungi, microalgae and plants supply reductants and ligands, as well as mac-

romolecular matrices that control precursor conversion, nucleation and surface capping (Adeleke et al., 2024; Iravani & Varma, 2020). Second, once introduced into the environment, the particles become regulatory stressors or functional agents that alter plant physiology and metal bioavailability, as well as microbial community structure and soil biogeochemistry (Kamwal et al., 2024).

These two directions of causality define the conceptual architecture of the review. The first concerns the molecular and biochemical mechanisms of nanoparticle formation. The second covers the regulatory consequences of particle exposure in the coupled plant–rhizosphere microbiome–soil system. Treating them separately prevents the review from becoming a catalogue of synthesis protocols or remediation efficiency values, and makes it possible to appraise critically both the mechanisms and the strength of evidence, as well as the ecological context.

Several unresolved problems make such an approach necessary. Biosynthesis mechanisms are often inferred from FTIR bands, pH shifts or correlations of enzyme activity without causal intervention. Toxicological findings are inconsistent across organisms and matrices. Field studies are far less numerous than laboratory ones, and comparative life-cycle assessment of biological versus conventional synthesis remains rare (Komárek, 2024). A mechanistic synthesis must therefore clearly separate what has been demonstrated directly from hypotheses supported by indirect data.

The aim of the review was to systematise the molecular and biochemical mechanisms of biogenic synthesis of metallic and metal-oxide nanoparticles, to analyse the demonstrated regulatory interacti-

ons in the plant–microbiome–soil system, to separate direct evidence on biogenic particles from extrapolations based on engineered nanomaterials, to assess the consequences for non-target biota, and to define the conditions for an environmentally responsible transition from laboratory models to field application.

The review focuses on metallic and metal-oxide nanoparticles obtained with the participation of bacteria, microalgae, endophytic fungi or plant extracts, and on their interactions with plants, rhizosphere microorganisms and the soil matrix. Only studies in which the origin of the particles and the biological or remediation outcome could be traced within a single experimental system were included in the direct line of evidence. Data on particles of undefined origin were used as contextual information, and nanoscale zero-valent iron (nZVI) only as a separate engineered comparator for electron-transfer, ageing, passivation and microbial reactivation processes. Medical delivery systems, food and cosmetic applications, polymeric and lipid nanoparticles, and antimicrobial studies unrelated to the plant–microbiome–soil continuum were left outside the scope of the review.

Literature search and critical synthesis

The study was designed as a narrative critical review intended to integrate mechanistically heterogeneous biochemical, physiological, microbiological and ecotoxicological evidence. It was not conceived as a systematic review of intervention efficacy, and therefore no formal meta-analysis or PRISMA flow diagram was applied. Quantitative pooling was inappropriate because of differences in nanoparticle composition, synthesis routes, particle characterisation, dose metrics, matrix properties, contaminant types, exposure duration and endpoints. The search was carried out in PubMed/MEDLINE, Web of Science Core Collection, Scopus, ScienceDirect and Google Scholar; the last update was performed on 12 July 2026. The main interval covered January 2018 – July 2026; earlier works were included if they defined nucleation theory, redox chemistry or a primary mechanistic experiment. Four blocks were used: (“biosynthesized nanoparticles” or “biogenic nanoparticle synthesis” or “green synthesis mechanism”) and (reductase or glutathione or polyphenol or nucleation); (“biogenic iron oxide nanoparticles” or “biosynthesized selenium na-

noparticles”) and (plant or soil or rhizosphere or microbiome); (“nano-bioremediation” or “nano-phytoremediation”) and (soil or plant) and (mechanism or ecotoxicity); (“nanoscale zero-valent iron” or nZVI) and (soil or rhizosphere) and (ageing or passivation or microbiome). Peer-reviewed primary studies and critical reviews with verifiable bibliographic metadata were included if the study addressed particle formation or transformation, their interaction with plants, microorganisms or soil, or their impact on non-target biota. Conference abstracts, dissertations, non-peer-reviewed reports, works without an identified nanomaterial and studies outside the conceptual scope were excluded. Duplicates were normalised by DOI, after which title, abstract and full-text appraisal were performed. Fifty-four publications were retained for the thematic synthesis. Numerical results were treated as context-dependent observations rather than directly comparable effect estimates.

The search blocks were adapted to the syntax of each database without altering the key concepts. PubMed was used for biomedical and molecular mechanisms, Web of Science and Scopus for interdisciplinary citation searching, ScienceDirect for full-text refinement of experimental detail, and Google Scholar only for forward and backward citation tracking. Records found solely in Google Scholar were included only after confirmation of the DOI and the publisher page.

Coding was performed according to predefined fields: biological platform, particle composition and origin, precursor, size and coating, matrix, dose, control variants, biological or remediation outcome, type of mechanistic evidence and principal limitation. Where a publication did not permit the particle effect to be separated from the action of the soluble ion or of the biological extract, no causal level above III was assigned.

Mechanistic claims were stratified into four levels. Level I covered genetic interventions, reconstituted systems or direct tracing of the causal process; Level II – consistent functional results confirmed by independent methods and appropriate controls; Level III – associative or indirect data; Level IV – conceptual extrapolation across species, matrices or particle classes. Causal verbs were applied only to Level I. Evidence level was assigned to an individual claim rather than to the publication as a whole; a study could support different claims at different levels.

Table 1
Hierarchy of mechanistic evidence applied in the review

Level	Criterion	Typical approaches	Permissible interpretation
I – direct causal	A specific alteration of the putative mechanism changes the outcome under appropriate controls	Gene knockout or knockdown; selective inhibition with rescue of the effect; reconstituted purified system; direct tracing of electrons or products	The mechanism mediates or causes the effect in the system studied
II – strong functional	Several independent functional measurements support the mechanism, but causality is not fully isolated	Kinetics and dose dependence; direct product determination; orthogonal spectroscopic or biochemical methods; appropriate negative controls	The data convincingly support involvement of the mechanism
III – associative or indirect	A consistent association is observed without mechanism-specific intervention	Correlations of enzyme activity; transcriptomics without functional validation; FTIR or XPS identification; pH shifts; morphological observations	The effect is consistent with the mechanism but does not demonstrate it
IV – conceptual	The mechanism is transferred from an analogous system or inferred from general consistency	Extrapolation from reviews; analogy between species or nanomaterials; ecological correlation without molecular verification	The mechanism is a working hypothesis requiring direct testing

Note: the evidence level refers to a specific mechanistic claim, not to the overall quality of the publication.

The principal limitations were the narrative design, the uneven representation of particle classes, the predominance of model and pot systems, and the absence of a common dose–effect metric. The search was not intended to estimate a pooled effect size and does not guarantee the completeness of a systematic review.

Reductive formation of elemental nanoparticles

A defining feature of biological synthesis is that the same pool of biomolecules may participate both in precursor conversion and in the stabilisation of newly formed nuclei. Reductants and capping agents jointly influence particle size, morphology and reactivity, as well as surface charge (Alabrahim et al., 2025; Nain et al., 2025). For elemental nanoparticles, the available data can be organised into three interacting redox routes, whose relative contribution depends on the biological agent, the precursor and the reaction conditions (Bityutsky

et al., 2020). The thermodynamic basis of reduction is the potential difference between the metal ion/elemental metal couple and the biological electron donor. Ions with favourable potentials, notably Ag⁺ and Au³⁺, may be reduced by NAD(P)H or phenolic groups; in a reconstituted system, NADPH formed AgNPs without nitrate reductase (Hietzschold et al., 2019). Oxyanions such as selenite often require a thiol-mediated or enzyme-supported route. The identity and chemical speciation of the precursor should therefore be stated explicitly: “metal reduction” is not a universal reaction independent of pH, ligands and oxidation state.

Enzymatic route

The involvement of nitrate reductase in nanoparticle formation by microorganisms or fungi is often inferred from measured enzyme activity, NAD(P)H availability and spectroscopic changes. In most such

studies the evidence remains at Level III, because the enzyme was not selectively removed from the system with subsequent rescue of the effect (Adeleke et al., 2024; Sahu et al., 2025). Stronger causal evidence has been obtained for biogenic selenium formation: disruption of fumarate reductase function in *Enterobacter cloacae* substantially decreased selenite conversion, which supports a Level I mechanism (Song et al., 2017). For thioredoxin reductase and glutathione reductase, mainly functional or correlative evidence of Levels II–III is available (Song et al., 2017; Martínez et al., 2020). For this reason, strain-dependent selenium conversion by probiotic lactobacilli and *Bacillus* species cannot be regarded as evidence for the involvement of a single universal reductase (Tymoshok et al., 2025).

Thiol-mediated route

Selenite can react with reduced glutathione to form selenodiglutathione (GS–Se–SG), which is further converted into elemental selenium, while oxidised glutathione is regenerated through NADPH-dependent metabolism (Martínez et al., 2020). Correlations between glutathione reductase activity and selenite conversion support the involvement of this loop, but without selective inhibition or genetic intervention they remain Level III evidence. Functionally, the route couples detoxification of the oxyanion with the formation of a less soluble selenium nanophasse.

Polyphenol–flavonoid route

In plant extracts, polyphenols and flavonoids may donate electrons during the oxidation of hydroxyl or catechol groups to quinone- or carbonyl-containing products. Phenolic, protein and tannin components are subsequently adsorbed onto the particle surface and provide steric or electrostatic stabilisation (Alabrahim et al., 2025). FTIR bands, total antioxidant activity and pH shifts are indirect Level III indicators rather than direct identification of a specific reductant. Attribution at Levels I–II requires fractionation, quantification of oxidation products, and depletion or add-back experiments with individual components.

Hydrolysis–precipitation–mineralisation route for metal oxides

The formation of metal-oxide nanoparticles cannot always be described as reduction of a metal ion to the elemental state. In Fe and related systems, biological ligands and local pH promote hydrolysis of aqua complexes, formation of metal-hydroxide precursors, olation or oxolation, dehydration and crystallisation of an oxide or oxyhydroxide phase. Proteins, polysaccharides, extracellular polymeric substances and polyphenols coordinate ions, restrict growth and form a surface coating. The field consequences of such mineralisation and ageing have been confirmed for green-synthesised iron oxides during long-term Cd stabilisation in soil (Lin et al., 2019a).

Demonstrating the hydrolysis–precipitation–mineralisation route requires more than identification of the final phase. Time-resolved measurements of precursor speciation, pH and oxidation state are needed, together with X-ray diffraction, electron microscopy and surface-sensitive spectroscopy. Studies of phytogenic iron oxides show that surface groups and Fe phases can support Cd sorption and co-precipitation, but do not demonstrate an identical mechanism for all plant extracts (Lin et al., 2019a; Andrade-Zavaleta et al., 2022). Without an abiotic extract control and a non-nanoscale analogue, attribution of “biogenic” oxide formation largely remains at Level III.

Nucleation, growth and biomolecular capping

Irrespective of the precursor conversion route, particle formation proceeds through supersaturation, nucleation, crystal or cluster growth and stabilisation. Temporal separation of nucleation and growth is critical for size control: a short nucleation burst followed by diffusion-limited growth usually yields a narrower size distribution than prolonged overlap of nucleation and growth (Thanh et al., 2014). Rapid precursor conversion may generate many small nuclei, whereas slow-

er conversion favours the formation of fewer, larger particles. Adsorption of proteins, polysaccharides, extracellular polymeric substances and phenolic compounds restricts further growth and fixes surface charge and interfacial reactivity.

The variables that are usually controlled have a direct biochemical meaning. pH alters precursor speciation, protonation of donor groups and surface charge. Temperature accelerates reaction kinetics within a limited range but may denature enzymes or thermolabile phytochemicals (Tymoshok et al., 2019). Precursor concentration and the amount of biological reductant determine supersaturation and the reductant/ion ratio, whereas reaction time controls the completeness of conversion and ageing (Vanlalveni et al., 2021). Reproducibility therefore requires quantitative control of both the physico-chemical conditions and the composition of the biological agent.

Critical interpretation of mechanistic evidence

Stratification of evidence changes the interpretation of frequently reproduced synthesis schemes. In a controlled system, NADPH reduced silver ions in the absence of nitrate reductase, whereas addition of the enzyme decreased the reaction rate (Hietzschold et al., 2019). In that system the effective electron donor was the cofactor, not the enzyme. In each case the mechanism depends on the strain and species of the organism, as well as on the precursor and the reaction conditions. FTIR identification, pH shifts and correlations of enzyme activity should generate testable hypotheses but should not replace genetic, kinetic or biochemical causal experiments.

Biological platforms as determinants of nanoparticle properties

Choosing a biological platform means choosing a characteristic combination of reductants, ligands, intracellular or extracellular localisation, nucleation kinetics and downstream purification requirements. Platform identity therefore affects both reproducibility and functional properties (Table 2).

Bacteria. Bacterial synthesis relies on reductases, NAD(P)H-dependent metabolism, thiol systems, proteins and extracellular polymeric substances (Tsekhmistrenko et al., 2021). Strain specificity creates opportunities for biological selection and process optimisation, but intracellular products may be difficult to recover, and mechanistic attribution often remains inferential (Iravani & Varma, 2020; Tymoshok et al., 2023).

Microalgae. Phyconanotechnology combines photoautotrophic biomass formation with extracellular polymeric substances, pigments, proteins and polysaccharides capable of converting the precursor and stabilising the particles (Chan et al., 2022). Light dependence can be mechanistically informative: extracellular material of *Graesiella emersonii* supported silver nanoparticle formation more efficiently under illumination than in darkness, which is consistent with coupling to photosynthetically generated reductants (Do et al., 2025). At the same time, light intensity, pH and medium composition substantially affect batch-to-batch variability.

Endophytic fungi. Fungal systems tolerate metal stress and secrete substantial amounts of extracellular proteins and low-molecular-weight redox mediators. Extracellular synthesis may simplify product recovery, and secreted quinones have been proposed as electron shuttles in reductase-associated routes (Durán et al., 2005). However, the functional contribution of a specific reductase is often inferred indirectly, and particle yield and properties remain species- and strain-dependent (Adeleke et al., 2024; Manganyi et al., 2024).

Plant extracts. Cell-free synthesis using plant extracts does not require the maintenance of living cultures and allows agricultural residues to be used as feedstock. Polyphenols, flavonoids, terpenoids, reducing sugars, proteins and tannins can provide a coupled conversion and capping system under mild conditions (Alabrahim et al., 2025). The same chemical diversity creates the most pronounced reproducibility problem: extract composition depends on plant species and organ, on season and growth conditions, and on the extraction procedure. Chemical standardisation of the extract is therefore a prerequisite for mechanistic interpretation and scale-up.

Table 2
Biological platforms of nanoparticle formation: mechanisms, functional advantages and limitations

Platform	Reducing or stabilising components	Typical route and localisation	Functional advantage	Principal technological or evidential limitation
Bacteria (Iravani & Varma, 2020; Tymoshok et al., 2023)	Reductases, NAD(P)H, glutathione, proteins, EPS	Enzymatic and thiol-mediated conversion; intracellular or extracellular	Strain specificity and potential for biological selection	For many strains the mechanism remains inferential; the intracellular product requires complex recovery
Microalgae (Chan et al., 2022; Do et al., 2025)	Photosynthetic pigments, EPS, proteins, polysaccharides	Light-dependent extracellular conversion; EPS promote conversion and stabilisation	Photoautotrophic cultivation and utilisation of carbon dioxide	Sensitivity to light, pH and medium composition; polydispersity
Endophytic fungi (Durán et al., 2005; Adeleke et al., 2024)	Secreted redox proteins, reductases and quinone mediators	Predominantly extracellular enzyme-associated conversion	Metal tolerance and comparatively simple product separation	Species and strain dependence; the causal role of individual enzymes is often unverified
Plant extracts (Alabrahim et al., 2025)	Polyphenols, flavonoids, terpenoids, sugars, proteins and tannins	Cell-free redox conversion or mineralisation with simultaneous capping	Operational simplicity, mild conditions and available biomass, including agricultural residues	Batch-to-batch variability and the need for chemical standardisation of extracts

Regulatory mechanisms in the plant–microbiome–soil system

The rhizosphere is the central reactive interface of particle activity. Root exudates alter pH and redox potential, form complexes with ions, and influence aggregation, dissolution and the surface corona. For biogenic particles, direct evidence of this loop is so far limited to a

few systems; the strongest data have been obtained for bacterial FeO nanoparticles in contaminated soil and for SeNPs synthesised by rhizosphere selenobacteria (Manzoor et al., 2021; Sun et al., 2024). In Figure 1, solid lines indicate direct or strong functional links, and the dashed line indicates model extrapolations from engineered nZVI.

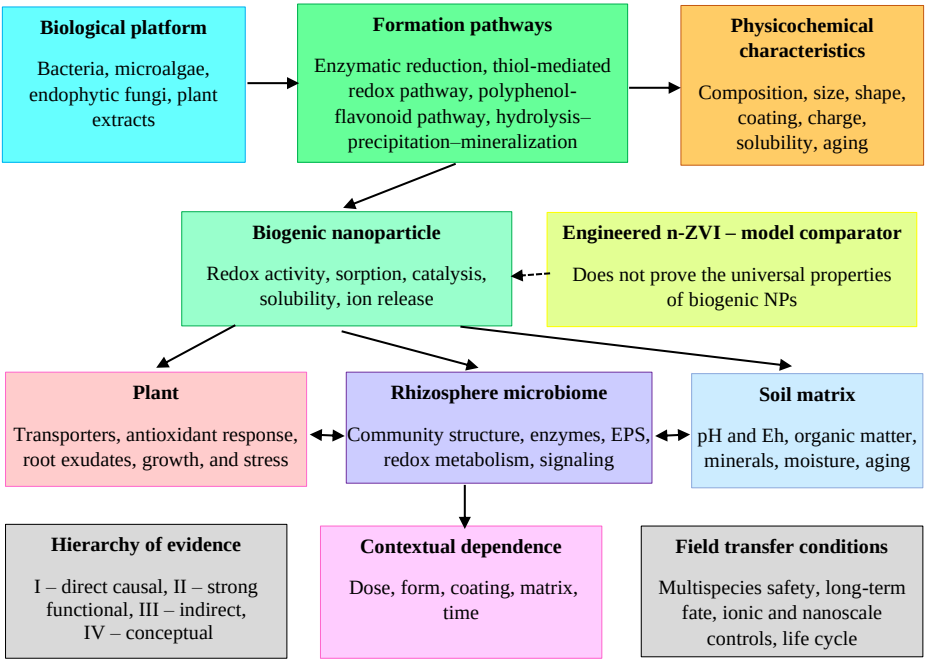


Fig. 1. Evidence scheme of biogenic nanoparticle formation and regulatory interactions in the plant–microbiome–soil system: solid arrows denote direct or strong functional evidence; the dashed arrow denotes the use of engineered nZVI solely as a model comparator of ageing and electron transfer. EPS – extracellular polymeric substances; Eh – redox potential

Regulation in the nanoparticle–plant direction

Nanoparticles affect plants through changes in contaminant availability and nutrient status, transporter expression and cellular redox balance. Toxic cations enter through the transport systems of essential elements, notably the NRAMP, ZIP/IRT1, HMA and YSL families (Tao & Lu, 2022). In Cd-contaminated saline soil, FeO nanoparticles synthesised by *Pantoea ananatis* reduced Cd uptake by wheat and altered nutrient balance; this is strong functional evidence for a specific system, but not a universal effect of iron oxides (Manzoor et al., 2021).

At the same time, particles may induce oxidative stress through surface redox cycling, structural defects and partial dissolution (Kessler et al., 2022). Plant responses include activation of superoxide dismutase, catalase and ascorbate peroxidase, changes in glutathione metabolism and lipid peroxidation. Whether these changes enhance tolerance or indicate toxicity depends on dose, coating, particle age,

exposure duration and soil conditions. Positive results for biogenic FeO nanoparticles cannot be transferred to other compositions without ionic, non-nanoscale and extract controls (Manzoor et al., 2021; Badamasi et al., 2026).

Regulation in the nanoparticle–microbiome direction

Rhizosphere microorganisms determine a substantial part of remediation efficiency and are themselves sensitive to particle exposure. Plant growth-promoting bacteria can bind metals with siderophores and extracellular polymers, produce auxins and solubilise phosphates, and express 1-aminocyclopropane-1-carboxylate deaminase, reducing stress ethylene and altering metal uptake (Sun et al., 2022; Karnwal et al., 2024). Arbuscular mycorrhizal fungi extend the effective rhizosphere through extraradical hyphae and immobilise metals via glomalin-related proteins, sorption and local pH changes (Mitra et al., 2024).

Particles may restructure rhizosphere communities by altering substrate availability, membrane stress and local redox conditions. The most convincing direct example has been obtained for SeNPs synthesised by selenobacteria associated with maize roots: soil assays, synthetic communities and multi-omics data linked particle biosynthesis with dose-dependent recruitment of *Bacillus* and improved plant status (Sun et al., 2024). For green-synthesised iron oxides, long-term incubation altered bacterial community structure together with Cd fractionation, but the causal contribution of individual taxa was not isolated (Lin et al., 2019a). Soil enzyme activity should be interpreted with account for possible analytical interferences.

Biological feedback on nanoparticle transformation

Roots and microorganisms actively modify particle fate. Root exudates may complex released ions, stabilise or destabilise colloids and alter surface charge. Microbial EPS form an in situ eco-corona, and metabolism changes local pH, Eh and oxygen availability. For SeNPs, a bidirectional signalling loop has been demonstrated in which root-derived p-coumarate regulated rpoS-dependent particle biosynthesis by selenobacteria, while the particles promoted the recruitment of beneficial bacteria (Sun et al., 2024). This is Level I–II evidence for a specific system, whereas transfer of the mechanism to other particles remains at Level IV.

Control of bioavailability and ageing by the soil matrix

Soil pH, mineral composition, organic matter, ionic strength and moisture determine particle transport and transformation. During long-term incubation, green-synthesised iron oxides shifted Cd from exchangeable and carbonate-bound fractions into more stable forms, together with maturation of Fe minerals and restructuring of the bacterial community (Lin et al., 2019a). For SeNPs, modelling and soil–plant experiments likewise indicate a joint influence of particle size, soil properties and biological activity on bioavailability (Li et al., 2024a). An effect established in water therefore cannot be extrapolated directly to soil.

Context dependence and non-monotonic responses

Biological interactions are not inherently synergistic. The effects of nanomaterials are often non-monotonic or hormetic in character (Iavicoli et al., 2018). For engineered nZVI, reduced mycorrhizal colonisation and decreased microbial biomass and enzyme activity have been shown at particular doses and soil conditions (Anza et al., 2019; Cheng et al., 2021). These findings are not direct evidence of the toxicity of biogenic particles, but they define the mandatory control variants: the ionic precursor, a non-nanoscale analogue, a metal-free biological extract, and comparison of equal mass and surface-area doses.

Engineered nZVI as a model comparator of ageing and bio-abiotic coupling

nZVI does not automatically belong to biogenic nanoparticles and is not used in this review to demonstrate their biological action. It is considered separately as a well-studied model of how soil and microorganisms modify abiotic electron transfer. The core–shell structure combines the Fe⁰ electron donor with an oxide-hydroxide surface that supports sorption, co-precipitation and electron transfer. The dominant route depends on the contaminant: Cr(VI) may be reduced to less mobile Cr(III), chlorinated compounds may undergo reductive dechlorination, and metal cations may be sorbed or co-precipitated (He et al., 2023; Li et al., 2024b; Liu et al., 2024a).

Low electron selectivity is a key limitation. Reducing equivalents are consumed by water and oxygen, as well as by non-target ions, while growth of the oxidised shell impedes electron transfer (Zhou et al., 2022). Sulfidation can suppress parasitic hydrogen evolution, whereas biochar supports or magnetite-containing composites can improve dispersion, sorption and Fe(II)/Fe(III) cycling (Lang et al.,

2022; He et al., 2023; Liu et al., 2024b). These modifications improve efficiency in selected model systems but do not demonstrate universal superiority.

Ageing of nZVI causes aggregation and conversion of the surface into secondary Fe minerals. Iron-reducing and dechlorinating microorganisms can partially reduce Fe(III)-containing surface phases and sustain electron-transfer capacity (Dong et al., 2019). This is a useful model for generating hypotheses about the ageing of biogenic Fe-containing particles, but differences in the initial phase, biomolecular coating and reactivity do not permit direct transfer of the mechanism. Field efficiency of nZVI is constrained by passivation, heterogeneous transport and the trade-off between reactivity and biological stress (Liu et al., 2022; Pan et al., 2024; Komárek, 2024).

Dose-dependent and ecotoxicological effects on non-target biota

Oxidative stress is a recurrent molecular denominator of nanomaterial toxicity. Reactive oxygen species may be generated directly in surface reactions and indirectly through dissolution and release of metal ions (Kessler et al., 2022; Reidy et al., 2013). The consequences include lipid peroxidation and protein oxidation, mitochondrial dysfunction and DNA damage. Particle-specific effects should be separated from the toxicity of released ions. For silver nanoparticles, intracellular dissolution in acidic compartments may make Ag⁺ release a substantial component of the biological response, although its relative contribution depends on particle size, coating and dissolution kinetics (Reidy et al., 2013).

Non-monotonic dose responses complicate the definition of a universal threshold. Particle size, morphology, coating and ageing alter both exposure and reactivity (Iavicoli et al., 2018). Matrix effects are equally important: nZVI usually reacts more predictably in water than in soil, where mineral and organic surfaces compete for reactive sites and co-contaminants modify immobilisation (Gil-Díaz et al., 2020; Komárek, 2024).

Safety conclusions also depend on the test organism. In *Eisenia fetida*, exposure to silver nanoparticles induces oxidative and molecular stress responses partly similar to the effects of soluble silver, which supports a substantial ionic contribution (Tsyusko et al., 2012). nZVI may decrease microbial biomass and activity (Anza et al., 2019), suppress mycorrhizal colonisation (Cheng et al., 2021) and alter earthworm endpoints, even where combined treatments reduce mobile metal fractions (Tang et al., 2024). Classical plant stress responses to metal toxicity additionally depend on transport and sequestration, as well as on antioxidant regulation (Ovečka & Takáč, 2014). An invariant ranking of the sensitivity of microorganisms, invertebrates and plants cannot therefore be assumed.

Evidence gaps and conditions for field translation

Inconsistency between studies has systematic causes: different matrices, ageing, incomparable dose units, undefined surface coating and analytical interferences. For biogenic particles, an additional source of variability is the composition of the extract or culture medium. A minimal design should therefore include the precursor without the biological agent, the biological agent without the precursor, the corresponding soluble ion, a non-nanoscale analogue, and characterisation of the particles before and after contact with soil. Studies of nZVI under conditions approaching field complexity demonstrate the risk of an absence of benefit or of enhanced root stress through interaction with organic matter (Lacalle et al., 2018), but this result should be treated as a design warning rather than as a direct analogue for biogenic particles.

Field translation requires determination of particle composition, size, shape, surface charge, coating, dissolution and transformation; reporting of mass-based and surface-area-normalised dose; description of pH, Eh, organic matter, texture and moisture; multi-species testing and long-term monitoring. Primary studies already demonstrate the dependence of the outcome on biological origin, dose and soil context (Lin et al., 2019b; Manzoor et al., 2021; Sun et al., 2024). Regulatory assessment should combine mechanistic evidence, pre-

dicted safe concentrations, life-cycle analysis and comparison with non-nanoscale alternatives (Schwim et al., 2020). Table 3 presents

studies in which the experimental system allows a specific mechanistic conclusion to be traced.

Table 3
Primary studies directly supporting the key mechanistic conclusions of the review

System and material	Key control or intervention	Supported conclusion and level	Principal limitation	Study
Enterobacter cloacae Z0206; biogenic SeNPs	Δfrd mutant; growth control; determination of residual selenite	Fumarate reductase is functionally required for the major part of selenite reduction; Level I	A single strain; the mechanism is not automatically transferable to other bacteria	Song et al. (2017)
Reconstituted AgNO ₃ -NADPH-nitrate reductase system	NADPH without and with the enzyme; kinetics; TEM	NADPH can be a direct reductant of Ag ⁺ ; Level I	A cell-free system does not reproduce the composition of the secretome	Hietzschold et al. (2019)
Phylogenetic Fe oxides; Cd-contaminated soil; long-term incubation	Dose variants; Cd fractionation; Fe phases; bacterial profile	Cd stabilisation is associated with maturation of Fe phases and community restructuring; Level II	The causal contribution of individual microorganisms was not isolated	Lin et al. (2019a)
<i>Pantoea ananatis</i> -synthesised FeO NPs; wheat; Cd and saline soil	Particle-free control; NP characterisation; physiological and elemental indices	Reduced Cd uptake and altered antioxidant response; Level II	A single crop and a single soil system; no surface-area-normalised analogue	Manzoor et al. (2021)
Eucalyptus-mediated Fe ₃ O ₄ NPs; contaminated agricultural soil	Phase characterisation; dose experiments with Cr and Cd	Sorption and immobilisation of metals by green-synthesised oxides; Level II	Plant and microbiome were not assessed; high laboratory doses	Andrade-Zavaleta et al. (2022)
SeNPs of rhizosphere selenobacteria; maize; synthetic community	Dose-based soil assays; genetic and multi-omics data; signal reconstruction	SeNPs recruit beneficial bacteria, while root signals regulate biosynthesis; Level I–II	A specific selenium and plant-microbial context	Sun et al. (2024)
Engineered Fe ⁰ in soil and water	Ionic, microbial and matrix variants	Comparator of ageing, passivation and reactivation; Levels II–III	Not direct evidence for the properties of biogenic particles	nZVI studies

Note: the level refers to the claim presented, not to the overall quality of the publication. nZVI and particles without confirmed biogenic origin are designated as comparators and are not used to demonstrate universal properties of biogenic nanoparticles.

Conclusions

Biogenic nanoparticles in remediation are best regarded as components of a bidirectional regulatory loop, but the strength of evidence differs substantially between its arms. Biological platforms govern precursor conversion, nucleation, mineralisation and surface capping. Genetic and reconstituted biochemical experiments directly confirm the role of a specific reductant only in individual systems, whereas FTIR bands, pH shifts and correlations of enzyme activity remain indirect. Direct soil-biological data are most convincing for individual bacterially synthesised FeO nanoparticles and SeNPs, but do not yet cover the diversity of compositions, coatings and soils.

Practical efficacy and safety are determined by dose, size, surface, matrix and time. Engineered nZVI is useful as a model of electron selectivity, ageing and passivation, yet it is not a universal analogue of biogenic particles. Responsible field application requires standardised characterisation of particles and biological agents, ionic, extract and non-nanoscale controls, multi-species testing, long-term monitoring and life-cycle assessment. Laboratory contaminant-removal efficiency without confirmation of particle fate, stability of immobilisation and safety for soil biota is not sufficient evidence of environmental benefit.

The authors declare they have no conflict of interest.

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