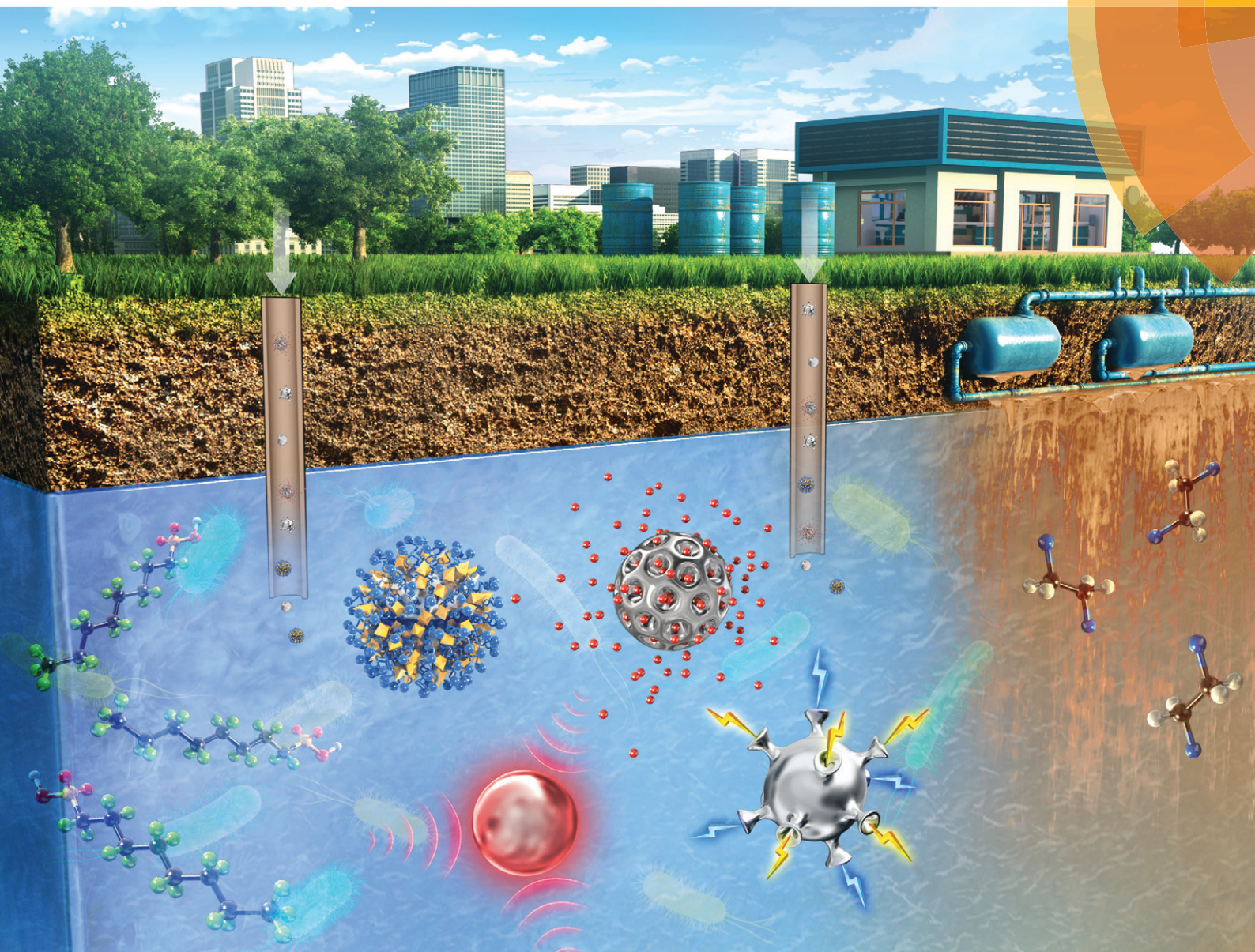


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In situ remediation of subsurface contamination: opportunities and challenges for nanotechnology and advanced materials



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In situ remediation of subsurface contamination: opportunities and challenges for nanotechnology and advanced materials

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Complex subsurface contamination domains and limited efficacy of existing treatment approaches pose significant challenges to site remediation and underscore the need for technological innovation to develop cost-effective remedies. Here, we discuss opportunities for nanotechnology-enabled *in situ* remediation technologies to address soil and groundwater contamination. The discussion covers candidate nanomaterials, applications of nanomaterials to complement existing remediation approaches and address emerging contaminants, as well as the potential barriers for implementation and strategies and research

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needs to overcome these barriers. Promising nanomaterials in subsurface remediation include multi-functional nanocomposites for synergistic contaminant sequestration and degradation, selective adsorbents and catalysts, nano-tracers for subsurface contaminant delineation, and slow-release reagents enabled by stimuli-responsive nanomaterials. Limitations on mixing and transport of nanomaterials in the subsurface are severe constraints for *in situ* applications of these materials. Mixing enhancements are needed to overcome transport limitations in laminar flow environments. Reactive nanomaterials may be generated *in situ* to remediate contamination in low hydraulic conductivity zones. Overall, nano-enabled remediation technologies may improve remediation performance for a broad range of legacy and emerging contaminants. These technologies should continue to be developed and tested to discern theoretical hypotheses from feasible opportunities, and to establish realistic performance expectations for *in situ* remediation techniques using engineered nanomaterials alone or in combination with other technologies.

Environmental significance

Subsurface contamination by both legacy pollutants and emerging contaminants continue to threaten groundwater resources. These groundwater pollutants are also a human health concern. There is need for advanced technical solutions to this vexing environmental problem. Nanotechnology can provide novel technical solutions, or can improve the efficacy of existing remediation strategies, to improve remediation efforts for subsurface contaminated sites.

Introduction

Groundwater and soil contamination by hazardous substances represent a significant technical and economic remediation challenge. The estimated liability of contamination in the United States (U.S.) is conservatively estimated to be between \$110 and \$127 billion, and at least 126 000 contaminated sites are deemed “intractable” with respect to being able to meet cleanup standards.¹ Similarly, the costs associated with cleanup of soil and groundwater in China are at least hundreds of billions of dollars.^{2–4} Several factors make subsurface remediation difficult, including the inability to characterize and effectively target source zones, the inability to monitor remediation performance, and the low efficiency of remediation agents that exhibit low or non-selective reactivity toward contaminants. In addition, poor mixing in the subsurface can limit contact between contaminants and remediation agents. Therefore, developing novel remediation technologies, as well as methods to enhance the performance of existing remediation approaches, are important parts of a multifaceted effort toward effective remediation of contaminated sites, protection of the public from harm, and for the conservation and restoration of natural resources and ecosystem services.

Over the last two decades, there have been significant research and engineering advancements in remediation of common soil and groundwater contaminants, such as petroleum hydrocarbons, chlorinated solvents, and heavy metals.^{5–8} Treatment technologies to remediate contaminated soil and groundwater work on one of the three following principles (or their combination): extraction (*e.g.*, pump and treat, surfactant flushing, air sparging/soil vapor extraction),^{9–14} transformation/degradation (*e.g.*, chemical oxidation/reduction, biodegradation),^{15–21} and sequestration and immobilization (*e.g.*, sorption).^{22–27} These are either performed *in situ*^{5,27–30} or *ex situ*.^{31–34} Nevertheless, subsurface contamination is highly complex and difficult to charac-

terize and cleanup (Fig. 1), which makes remediation and achievement of restoration goals very challenging. In particular, many toxic organic compounds and emerging pollutants are hydrophobic and difficult to withdraw from the subsurface, thus making methods relying on water flushing, extraction and treatment, such as ‘pump and treat’, mostly ineffective at achieving restoration. While ‘pump and treat’ approaches are effective for plume hydraulic control and containment, most efforts now focus on *in situ* treatment for source remediation and for reaching target levels of contaminants in groundwater.¹ Different domains associated with subsurface contamination (*i.e.*, types and phases of contaminants and medium properties) pose specific challenges that currently limit our ability to meet groundwater cleanup goals (*e.g.* drinking water standards) for *in situ* remediation in an economical manner and within a reasonable time frame.

Many sites have been impacted by multiple spills and contain many types of contaminants that must be treated simultaneously even though they may require different treatment conditions or materials (reagent) functions for effective remediation. For example, sites impacted by fuel spills containing monoaromatic hydrocarbons (requiring oxidation) and heavy metals (requiring reduction, adsorption or precipitation) can be difficult to remediate using a single approach for both classes of contaminants. Thus, remediation efforts have to offer broad applicability and/or multi-functionality to be effective. In addition, there are some contaminants of emerging concern (*e.g.*, per- and poly-fluoroalkyl substances-PFASs) that are not readily degradable with existing technologies.^{35–37} The subsurface environment is also dynamic, both geochemically (*e.g.*, a range of pH ionic strength, and redox gradients) and biologically (*e.g.*, a heterogeneous distribution of organisms or electron acceptors spatially and temporally available).^{38–40} Such changing conditions can affect the performance of remediation technologies while also posing technical difficulties in locating the contaminant source zone for treatment and effective implementation of monitoring

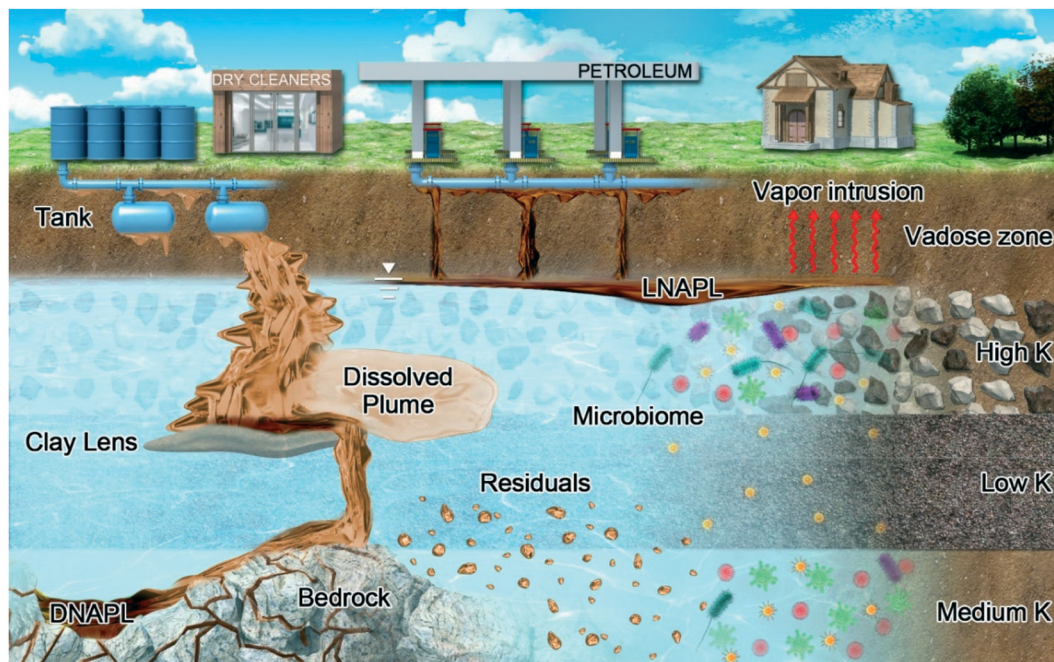


Fig. 1 Possible remediation and treatment domains in a contaminated subsurface environment. Organic contaminants are present as either dense or light non-aqueous phases (DNAPL and LNAPL), or as a dissolved contaminant plume. Contaminant mobility and the ability to emplace reagents depends highly on the hydraulic conductivity (K) of the aquifer medium. Low K regions, especially those in clay lenses are difficult to remediate due to the inability to deliver remediation agents to those regions. ENMs have potential to provide new remediation technologies, or to improve existing remediation technologies, for each domain.

systems. Monitoring costs can often be the most expensive part of remediation, due to long remediation time frames associated with monitored natural attenuation (MNA), pump and treat, and enhanced bioremediation techniques, which have a low cost of initial implementation.¹ Moreover, hydrogeological heterogeneity makes it difficult to deliver remediation agents to the desired locations. For example, *in situ* delivery of remediation agents, including engineered nanomaterials (ENMs), will generally follow flow paths of higher hydraulic conductivity; thus, their delivery to target contaminants in low conductivity regions that are surrounded by high conductivity zones is challenging. Many remediation technologies rely on the injection of reagents or redox manipulating materials (for *in situ* chemical oxidation or reduction or biostimulation).^{41–45} Limited transverse dispersion in a porous medium limits reagent mixing with contaminants, and vastly lowers efficiency and efficacy of *in situ* technologies. For example, the presence of (residual) dense non-aqueous phase liquid (DNAPL) or contamination source zones in low permeability inclusions (*e.g.*, in clay lenses) results in slow release of contaminants into the aqueous phase.^{46–49} Limited mass transfer then results in decreased bioavailability and impeded contaminant degradation, thus making the time to reach cleanup goals unreasonably long. These challenges indicate a demand for remediation alternatives that can provide exceptional reactivity while overcoming mass transfer limitations.

Nanotechnology has the potential to overcome some of these limitations and to improve both contaminant monitor-

ing and treatment (Fig. 2). The greatest opportunities for novel ENMs to improve subsurface remediation will come with the ability to design materials that can degrade highly recalcitrant compounds (where biodegradation alone is ineffective), that are highly selective for the target contaminants, are able to efficiently utilize the available treatment capacity of the material, that can provide multifunctionality to address mixed contamination issues, or those that can remain effective under dynamic biogeochemical conditions. Nano-enabled applications may also improve the performance of existing remediation technologies (*e.g.*, lowering the energy requirements for thermal treatment), provide better source zone characterization, faster source remediation by better management of residual contamination, and improve monitoring of remediation progress. However, it is important to note that nanotechnology-enhanced remediation alternatives will be subject to some of the same technical limitations as many conventional treatment technologies, including poor subsurface transport and heterogeneity of pollutants in the subsurface. Therefore, novel methods are needed to efficiently deliver engineered nanomaterials to contaminated zones and to leverage subsurface heterogeneity for effective remediation *e.g.*, delivering nanotechnology-enabled remediation agents to the source areas through the high conductivity layers in the subsurface.⁵⁰

The objectives of this tutorial review are to present key opportunities where engineered nanomaterials (ENMs) are likely to enhance *in situ* subsurface remediation, and to identify high priority research needs to realize more rapidly and

fully the benefits of nanotechnology for site remediation and monitoring. Realizing these benefits will require better tools to design and synthesize ENMs and novel approaches to deliver them effectively to the subsurface environment. Here, we present recent advances in nanomaterial design and delivery methods that are most likely to enhance the performance of *in situ* remediation.

Opportunities for advanced materials to enhance site remediation

Advances in material science and nanotechnology are now affording novel materials for enhancing *in situ* remediation of the most ubiquitous and persistent contaminants and for improving the ability to delineate source areas and monitor remediation progress (Fig. 3). The ability to design and synthesize multifunctional nanomaterials, which can simultaneously target multiple contaminants and exhibit higher selectivity toward contaminants relative to other matrix components (*e.g.*, H₂O and aquifer material), provides opportunities to significantly enhance the reactivity of materials designed for *in situ* remediation.⁵¹ The application of ENMs with tunable surface functionalities can help delineate the geophysical and hydrological conditions of the subsurface environment and report information about source zones.^{52–54} Composite nanomaterials that adapt to the surrounding environment and undergo structural changes in response to geochemical stimulants such as pH, temperature or redox changes⁵⁵ may further facilitate site investigation and improve the efficiency of sequestration/degradation of targeted contaminants. The design and synthesis of these advanced ENMs may be facilitated by supporting technologies such as computational design,⁵⁶ combinatorial libraries⁵⁷ and 3-D printing,⁵⁸ and through synthesis of polymers with specific pendant functional groups that can elicit required surface properties. The judicious assembly of building blocks comprised of small molecules and polymers through these ap-

proaches holds promise for new multifunctional and safe nanomaterials that are ideal for subsurface remediation with enhanced performance surpassing those enabled by current trial-and-error synthesis strategies. Given that the use of ENMs for *in situ* remediation involves direct releases to the environment, the choice of inexpensive, earth-abundant, and non-toxic elements or building blocks for ENM synthesis is essential. Such an approach would address regulatory considerations such as the precautionary principle as described in the EU Water Framework Directive (EU Water framework directive 2000/60/EC) with respect to groundwater discharges of ENMs.⁵⁹

Nanomaterials with multi-functionality

At remediation sites, the most ubiquitous and persistent chemicals of concern include heavy metals (*e.g.*, Cd, Hg, Pb), oxyanions containing As, Cr, Sb, and Se, chlorinated solvents, and other organic contaminants (*e.g.*, PFAS, polycyclic aromatic hydrocarbons (PAHs) including the more mobile nitrogen, sulfur, oxygen substituted heterocyclic compounds (NSO-PAH) and alkylated PAHs).⁶⁰ Multiple combinations of these contaminants are often present and cannot be remediated simultaneously with a single existing technology due to their dissimilar requirements for reagents, reaction conditions, and time. Organic contaminants are often sequestered through adsorption and/or degraded *via* redox reactions, while immobilization of heavy metals and metalloids occurs through adsorption and precipitation. Reduction, and sometimes oxidation, is desirable for reducing the bioavailability and toxicity of oxyanions. Current remediation methods are limited by their contaminant-specific efficacy and require sequential treatments with longer duration and higher energy input to attempt meeting clean up goals. ENMs can be designed to combine functions in a synergistic manner to concurrently target mixed contaminants and/or enable multiple remediation pathways (Fig. 3a).⁶¹ Hence, removal of

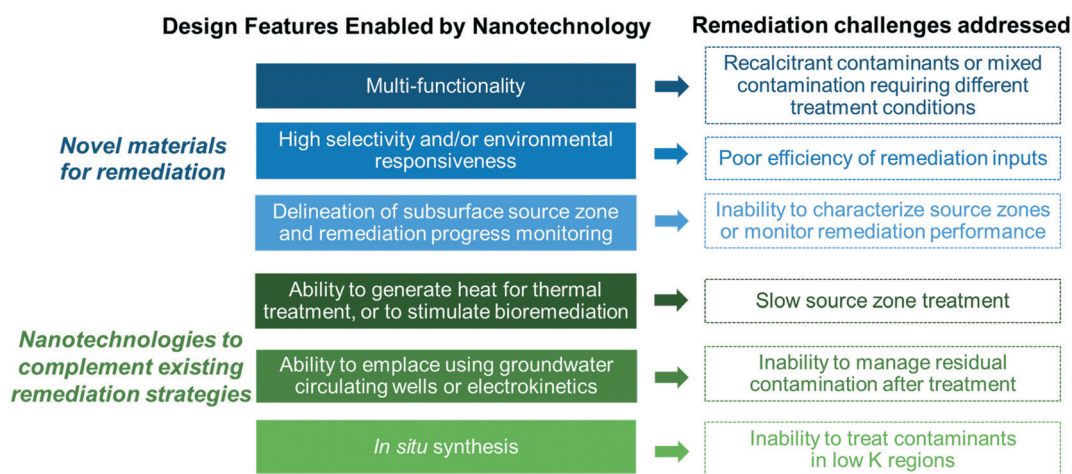


Fig. 2 Opportunities for nanotechnology-enabled solution to address remediation challenges. Novel materials could be designed to provide new strategies for remediation or to address emerging contaminants without feasible remediation alternatives, or to complement existing remediation technologies.

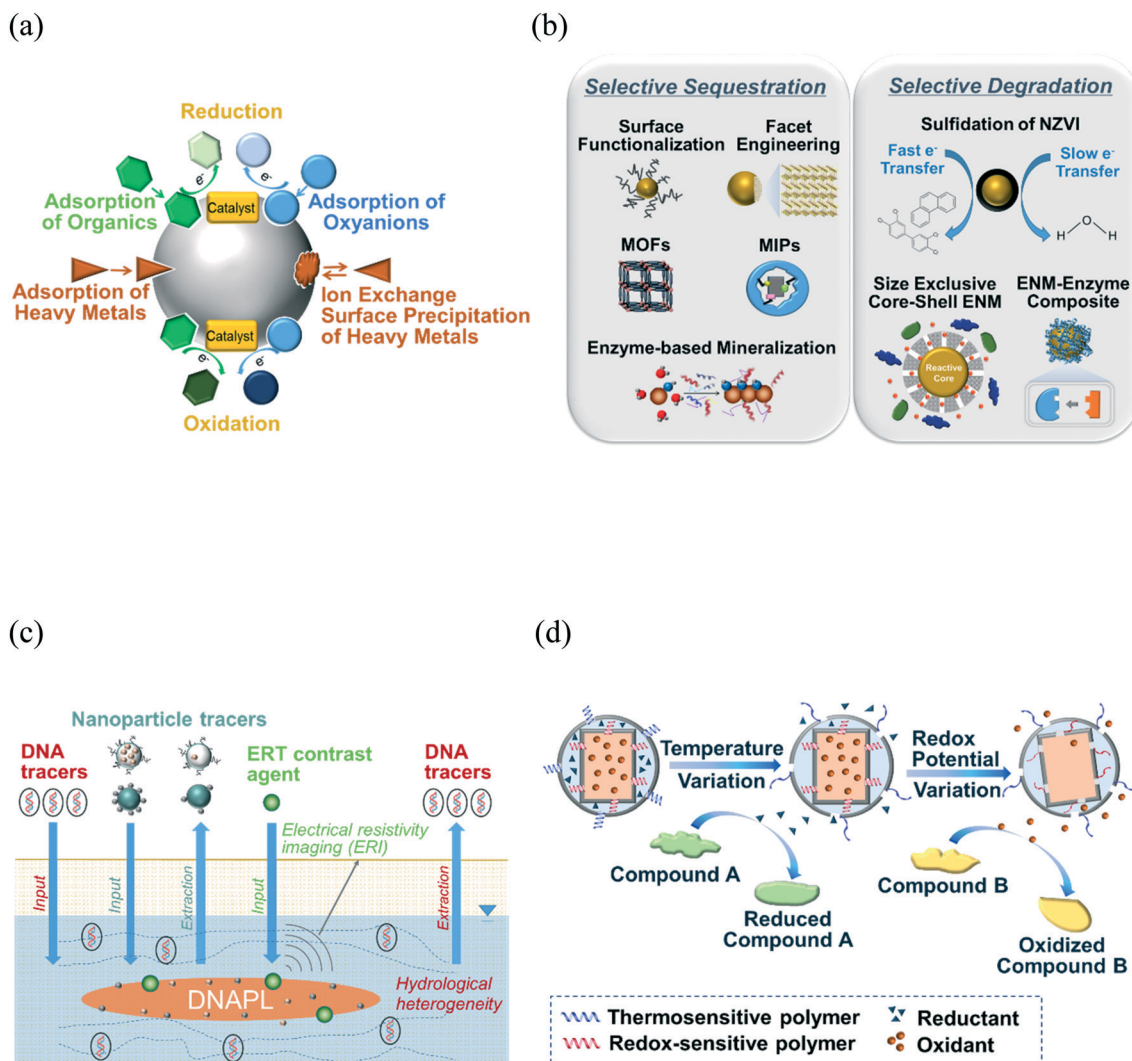


Fig. 3 Opportunities for engineered nanomaterials (ENM) to provide new *in situ* remediation technologies: (a) ENMs with multifunctionality can address mixtures of contaminants; (b) ENMs with high selectivity for contaminants can improve performance and their reactive lifetime; (c) nano-tracers to better delineate the distribution of contaminants in the subsurface; and (d) stimuli-responsive ENM that release reactants only when and where they are required.

a broad spectrum of contaminants in a single treatment phase could be realized.

ENM-enabled synergy between adsorption (or sequestration) and degradation offers the potential to concentrate and expose contaminants to elevated concentrations of reactive agents and enhance removal and/or transformation rates. For example, electron transfer to or from the target compound and free radical formation can both benefit from bringing the contaminants to the surface of ENMs. Thus, ENMs with sorptive as well as reactive functionalities are highly effective in surface-driven degradation of contaminants. In water and wastewater treatment, Fenton's reagent and other (photo- and electro-chemical) advanced oxidation processes (AOPs) take advantage of surface oxidation, where hydroxyl radicals are produced *in situ* on catalyst surfaces. For example, degradation of recalcitrant compounds, such as PFASs (with strong C–F bonds) can benefit from surface-mediated reactions using multiwalled carbon

nanotube supported TiO₂ (ref. 62) or single-atom Pt/SiC catalysis (whose synthesis method may be extended to other single-atom metal catalysts) for efficient C–F bond activation and defluorination.⁶³ These example catalysts used light activation, making them impractical for *in situ* applications, but they could be used in above-ground pump and treat schemes. It will be shown later how other stimuli that can be delivered into the subsurface may also be able to activate ENMs to enable *in situ* dehalogenation reactions.

Materials that can readily sequester contaminants, but have little ability to degrade them to non-toxic products could expand the number of reactive materials that may be useful for *in situ* remediation because sequestration obviates the need for rapid reaction. For example, surfactants adsorb organic compounds through hydrophobic interactions while adsorbing heavy metals through electrostatic attraction and chemical complexation. A core-shell micellar nanocoagulant

of 3-(trimethoxysilyl)propyl-*n*-octadecyldimethylammonium chloride effectively removed a diverse variety of organic and inorganic contaminants, such as perfluorocaprylic acid, fluoride, nitrate and total phosphorus, from water all at once.⁶⁴ Another nanocomposite, to improve the stability of the surfactant micelle arrays, was confined within the mesopores of an iron-based nanomaterial with a porous silica layer. This composite material successfully sequestered both acenaphthene and Cd(II) from the same aqueous solution. Remediation performance was robust over a wide pH range (4–9) and in the presence of natural organic matter as well as competitive divalent cations (*i.e.*, Ca²⁺, Mg²⁺).⁶⁵

Nanoscale zero-valent iron (NZVI) is the ENM that has received the most attention for *in situ* remediation. It is recognized for its strong reducing capacity ($E^0 = -447$ mV vs. SHE at STP),⁶⁶ but it may also induce Fenton's type oxidation of organics and metalloid oxyanions *via* Fe²⁺ released from the particle. For example, the combined addition of persulfate and NZVI leads to synergistic Cr(VI) reduction and phenol oxidation. Cr(VI) is reduced by NZVI to generate Cr(III) and dissolved Fe(II) ions, which activate persulfate to further oxidize phenol.⁶⁷ Moreover, when well dispersed, NZVI itself can induce multiple processes of adsorption, ionic exchange, oxidation, reduction, co-precipitation, and complexation. In batch experiments contaminated soil samples, a zeolite-supported NZVI simultaneously transformed Cd(II), Pb(II), and As(III) to their less toxic forms (*i.e.*, Cd(OH)₂, Pb⁰, and FeAsO₄).⁶⁸ Careful modulation of water chemistry, particularly pH, could facilitate the transition from competition to synergy among different reaction pathways.

Nanomaterials with high selectivity for contaminants

Another advantage of nanomaterials for subsurface remediation is their potential to be designed with high selectivity toward specific contaminants. Such designs could enable precision sequestration and/or selective degradation through a “catch and zap” strategy. Selectivity is highly desirable for several reasons. First, the reactivity or sorptive capacity of an injected nanomaterial is finite. A non-selective nanomaterial would be exhausted quickly by reacting with naturally occurring organics and background metals ions that are often present in much higher concentrations than the target contaminants. Reactive nanomaterials could also get rapidly exhausted if they react with water, as is the case for NZVI.⁶⁶ Second, limiting off-target reactivity can lower the amount of remediation agents required. Current *in situ* remediation technologies lack selectivity, which wastes treatment capacity. For example, advanced oxidation or *in situ* chemical oxidation (ISCO) reagents are largely consumed by non-target materials like soil organic matter.⁶⁹ Finally, selective removal of contaminants can avoid unintended consequences, such as the loss of soil function or the generation of toxic byproducts. Appropriately designed ENMs can selectively adsorb or degrade target pollutants without being consumed by water, or being interfered with by native soil constituents.

The selectivity of ENMs can be controlled by manipulating their physical structure (*e.g.*, pore structure, crystal facets) and surface chemistry (*e.g.*, surface acidity/basicity, charge, hydrophobicity/hydrophilicity), and by functionalizing their surfaces with ligands possessing molecular recognition abilities, such as aptamers, enzymes, peptides, carbohydrates, molecular imprinted polymers, or conductive materials (Fig. 3b).

Surface functionalization of magnetite particles with amine groups improves the selectivity of this ENM for Hg(II) when presented with an array of other divalent metals, including Co(II), Cu(II), Fe(II), Ni(II), Zn(II), and Mg(II).⁷⁰ Clay, functionalized with polysulfide, exhibits much higher affinity toward Cu(II) and Zn(II) compared to other transition metals, such as Co(II) and Ni(II) through metal-sulfur binding.⁷¹ Selectivity for heavy metal adsorption onto hematite nanocrystals can be modulated by facet engineering. When increasing the Mn dopant level, nano-hematite is transformed from isotropic polyhedral to {116}-faceted and {001}-faceted crystal structures, and such transformation can enable preferential adsorption of Cd(II) and Pb(II) on this nanomaterial.⁷² Facet-selective adsorption of different organic compounds, such as phenol and hydroquinone, can take place on Pt nanomaterial surfaces. Such selectivity may be determined by the electrostatic potential and geometric structure of the organic molecules.⁷³ A peptide induced mineralization process is also reported to selectively separate rare earth elements from various metal ions under environmental pH conditions. With the help of molecular simulations, this approach can be extended to selectively sequester other transition metals by designing proper macromolecules and chemical reactions.⁷⁴

For oxyanions, metal-organic frameworks (MOFs) offer an effective strategy for precise capture of target compounds from a complex matrix. In particular, careful modulation of the porous structure and the local binding environment of metal atoms greatly enhances the hydrolytic stability of MOFs under environmentally relevant conditions, an essential trait for groundwater remediation. For instance, a cationic europium(III)-based MOF is highly selective to chromate in the presence of a large excess of other anions in lake water and seawater (*e.g.*, Cl⁻, NO₃⁻, and HCO₃⁻).⁷⁵ A bismuth-based MOF demonstrated extremely high adsorption capacity for selenite, Se(IV), over its less toxic form Se(VI), in a wide pH range of 4–11 and in the presence of abundant environmentally relevant anions.⁷⁶ While these MOFs are highly selective, MOFs used for groundwater remediation will ultimately need to use earth abundant metals to be environmentally friendly and cost-competitive. Molecularly imprinted polymers (MIPs) also offers potential for improving the selectivity of ENMs. For example, a water-compatible MIP grafted onto porous graphene oxide materials selectively adsorbed bisphenol A (BPA) from river water containing other analogue molecules, such as tetrabromobisphenol A and 4-*tert*-butylphenol.⁷⁷

Compared to selective sequestration (*i.e.*, adsorption or precipitation), fewer approaches are available for designing nanomaterials to selectively degrade/transform contaminants.

A good example is partial sulfidation of NZVI that enables its preferential reactivity toward trichloroethene (TCE) over water.^{51,78} This has the potential to create NZVI with higher reactivity toward the target contaminant and a much longer reactive lifetime of the Fe⁰ core.^{51,78} Selective oxidation of organic contaminants is also possible. Phenol is selectively degraded over other organic contaminants, such as benzoic acid and ibuprofen, by nitrogen-doped nanospheres of carbonized polypyrrole through peroxymonosulfate activation.⁷⁹ This selectivity is a result of the differences in the ionization potentials of these different compounds. Only the organic molecules with an ionization potential below the metastable state of the nanocatalyst after electron transfer to the peroxymonosulfate molecules are readily degraded.⁷⁹ Alternatively, enzymes that are responsible for biodegradation of organic contaminants can be immobilized onto nanoparticles to synthesize composite materials. These nanocomposites exhibit substrate (*i.e.*, organic contaminant) specificity as well as higher activity and stability in complex matrices compared to free enzymes.^{80–82}

Given that non-aqueous phase liquid (NAPL) source zones are responsible for slow, but continuous release of contaminants into aquifers, introducing functional ENMs that can partition into the NAPL or to the NAPL–water interface can potentially achieve targeted degradation of the source zones, controlled displacement of the NAPL to enable its recovery, or decrease the rates of contaminant dissolution into groundwater. A number of ENMs (*e.g.*, polymeric, silica, metal ENMs functionalized with specific polymers) are being considered to improve enhanced oil recovery (EOR) by the oil and gas industry.⁸³ These ENMs partition onto oil–water interfaces to lower the interfacial tension, surface pressures at oil–water interfaces, or wettability of the formation rocks, to enable oil displacement. Furthermore, accumulation of naturally occurring nano- to micron-sized colloids of asphaltenes and resins at crude oil- and coal tar–water interfaces have been shown to dramatically reduce dissolution rates of PAHs from those NAPLs through alteration of the interfacial rheology.^{83,84} Thus ENMs designed to partition at the NAPL–water interface could be used to stabilize plume generation from NAPL source zones. ENMs that are reactive to target NAPL constituents (*e.g.*, PAHs, chlorinated hydrocarbons) and are engineered to preferentially attach at NAPL–water interfaces will allow for efficient degradation of source zone contaminants. For example, NZVI, surface functionalized to partition onto a butanol–TCE NAPL–water interface showed significantly higher degradation rates of TCE compared to parallel systems where the NZVI was only suspended in the aqueous phase.⁸⁵ Enhanced source zone remediation generally decreases the duration of the expansion and steady-state stages of dissolved plumes,⁸⁶ and facilitates eventual plume shrinkage as a result of natural attenuation. However, these nanomaterial-enhanced approaches have only been evaluated at the bench-scale and will need to be verified through field experiments to assess their feasibility and cost effectiveness.

Nano-“tracers”

Physical, chemical, and hydrogeological heterogeneity in the subsurface affects contaminant distribution and the ability to deliver ENMs to the location of the contaminants (Fig. 1). The ability to map physical (*e.g.*, preferential flow paths) and chemical (*e.g.*, areas with high or low organic matter or reactive mineral species) heterogeneity in the subsurface would vastly improve the efficacy of remediation. Chemical tracers, such as KBr, are used to determine total porosity as they rapidly diffuse from fractures into the surrounding matrix, while colloidal tracers travel faster through the aquifer due to decreased diffusion into low permeability regions and pore size-exclusion. The combined application of nanomaterials and chemical tracers offers an efficient way to assess the heterogeneity and the degree of preferential flow in subsurface environments according to the differential transport behavior of the two tracers.^{87,88} Ideally, such nano-tracers are uncharged and coated with hydrophilic ligands so that they travel through aquifers without aggregating or sticking to mineral surfaces.⁸⁹

Hydrological tracers, such as silica, bromide, and fluorescent molecules are often ubiquitous in natural settings^{90,91} and are subject to dilution effects.^{92,93} The detection sensitivity of these tracers are relatively low due to environmental background interferences. Single or double stranded DNA grafted onto or incorporated into nanomaterials is a recently proposed tool to overcome this limitation when evaluating hydrological conditions (Fig. 3c).⁹⁴ Attachment of DNA onto ENM surfaces protects DNA from degradation by chemicals, enzymes, and microorganisms in the environment during hydrological surveys.⁹⁴ The high specificity and low detection limits for DNA analysis enables precise tracking of nano-tracers with minimal background noise. Furthermore, the infinite diversity of DNA sequences allows simultaneous application of multiple distinguishable tracers with tunable migration behavior, which can be used to map spatial heterogeneities of hydraulic or chemical properties. The efficacy of DNA-silica nanocomposites in imaging subsurface reservoirs was recently validated in the field. This study demonstrated that a “multisource-multi-receiver” nanocomposite tracer can effectively characterize heterogeneous hydraulic conductivity fields.⁹⁵

NAPLs are a particularly persistent class of groundwater contaminant that can serve as a long-term (decades to centuries) source of contaminants to the groundwater. Light NAPLs (LNAPLs), such as benzene, toluene, ethylbenzene, and the xylenes (BTEX), and other hydrocarbons associated with fuels, tend to accumulate on the upper surface of groundwater, and are relatively easy to locate and treat (Fig. 1). In contrast, dense NAPLs (DNAPLs), such as chlorinated solvents, coal tar, and creosote are heavier than water and tend to migrate to and accumulate in deeper subsurface zones. Delineating the location and extent of DNAPL zones is extremely challenging, especially for complex and heterogeneous subsurface environments. This is true because DNAPL

migration is largely governed by the heterogeneity in permeability and pore geometry of the geologic formation; clay lenses may create preferential flow paths that can intercept and divert DNAPL flow (Fig. 1). Current techniques for characterizing DNAPL are costly (*e.g.*, drilling, sampling and laboratory analyses), time-consuming, and do not have sufficient spatial resolution. Finding residual DNAPL after source zone remediation is even more challenging due to lower contaminant mass residue and greater non-uniformity of the distributed DNAPL. Furthermore, inadequate delineation of DNAPL source zones or residuals (*i.e.*, pools and ganglia) prior to remediation can be the most dominant cause for failure of any remediation approach. Nanotechnology may provide a niche for DNAPL source zone delineation, in particular for subsurface environments containing fractured rocks, for which the applicability of conventional approaches, such as drilling, is limited.

Two nano-enabled approaches may prove to be successful for source zone delineation and DNAPL-residual characterization. The first approach involves the use of ENMs that are specifically designed with hydrocarbon detection abilities in oil-field rocks.^{53,54} Nanoparticles (consisting of oxidized carbon black as the core and polyvinyl alcohol as the shell) have been coated with a pre-selected hydrophobic compound and injected into the subsurface and then recovered and analyzed to assess the presence of hydrophobic compounds (*e.g.*, oil). The amount of the hydrophobic compound lost from the nanoparticles correlates with the amount of oil present in the subsurface.⁵⁴ A similar concept could likely work for DNAPL detection. The tracer nanoparticles can carry a sensing molecule or be tagged with a fluorescent hydrophobic coating that is quenched upon encountering DNAPL (Fig. 3c). This approach can be particularly useful for the characterization of DNAPL location and mass in fractured rocks, where most conventional techniques fail. Such a nano-enabled approach can provide a much higher spatial resolution for the contaminants, and is less likely to cause accidental migration of DNAPL (*e.g.*, drilling may penetrate clay lenses that prevent DNAPL from migrating down into deeper aquifer). Moreover, this approach may provide further benefits, such as site origin fingerprinting; in that different types of signaling components can be incorporated into the nanoparticles and each component may detect the presence or absence of a certain class of chemical to characterize the source composition.

The second nano-enabled approach that can potentially improve elucidation of DNAPL source zones is electrical resistivity tomography (ERT, Fig. 3c). ERT provides the capacity to map the resistivity structure of subsurface environments. Subsurface electrical resistivity is dependent on the type and arrangement of the various solid constituents, the composition of the pore fluid, and the local temperature. In general, DNAPLs are more resistive than water⁹⁶ and thus it is theoretically possible to utilize ERT to delineate and map DNAPL source zones. However, unless these zones have sufficient interfacial area, the electrical contrast can be too low to enable differentiation. NAPL-targeting nanoparticles, that ex-

hibit substantially different resistivity levels compared to water and other subsurface constituents, can potentially improve detection.

Stimuli-responsive nanomaterials

The ability to design and engineer stimuli-responsive materials can also lead to multifunctional and selective ENMs for site remediation. These “active and adaptive” nanomaterials can be designed to respond to environmental stimuli (*e.g.*, changes in pH, redox potential, or temperature) or to external stimuli (*e.g.*, microwave or radio frequency radiation) and provide targeted reactivity on-demand. For example, thermosensitive polymers, such as poly(*N*-isopropylacrylamide), can be utilized to embed reactive metallic nanoparticles to form composite materials that swell and expose reactive centers at low temperature, while shrinking and shielding the reactive centers at high temperature, so that overall reactivity is modulated by temperature changes.⁹⁷ These polymers that undergo conformational changes when heated have also been used to coat hollow and porous silica nano-cages containing a reactive material.⁹⁸ This nanocomposite material could be triggered to release encapsulated reagents by using low-frequency radio waves to raise the temperature. Furthermore, pH- and redox-sensitive polymers similar to those applied in drug delivery (where localized pH near cancer cells is lower than near healthy cells^{99,100}) could also be used to provide groundwater remediation agents that respond to localized conditions that occur in proximity to pollutants (*e.g.*, reduced dissolved oxygen, pH, redox potential). In addition, multi-stimuli responsive ENMs with multi-layer structures may be designed to enable treatment of various contaminants that degrade under different reactive processes. For example, a thermally triggered release of reducing reagent from an outer layer can be followed by a redox-triggered release of an oxidant from an inner layer. Once the contaminants susceptible to reduction have been degraded, the redox potential of the system can be raised to release the oxidant and attain oxidative degradation (Fig. 3d).

External stimuli could also be used to “activate” ENMs. For example, radio frequency waves can super-heat certain carbonaceous nanoparticles or metals (*e.g.*, iron carbide or magnetite).^{101–103} Such heating can initiate smoldering of heavy hydrocarbons.^{101,104} Iron nanoparticles have recently been functionalized to selectively bind and detect hydrocarbons in the subsurface,¹⁰⁵ and could be a first step prior to external ENM activation and initiation of hydrocarbon removal.

Using nanotechnology to complement existing remediation technologies

In some cases, small quantities of ENMs have tremendous potential to enhance the performance of several proven remediation strategies, especially when the existing technology

falls short of achieving cost-effective and efficient cleanup. A summary of the opportunities and feasibility of using ENMs to complement existing remediation approaches is included in Fig. 4 and in the following sections. While not comprehensive, it highlights areas where ENMs can improve current remediation approaches and reduce both time and cost.

Nano-enhanced biodegradation

Combining nanomaterials with bioremediation, either sequentially or simultaneously, can accelerate groundwater remediation. Physicochemical technologies, such as *in situ* chemical oxidation, thermal treatment, and surfactant flushing have worked well in combination with bioremediation as a ‘polishing step’.^{106–108} Numerous studies have shown that such physicochemical processes can transform recalcitrant and/or poorly bioavailable contaminants into more soluble and more biodegradable byproducts, thus enhancing microbial participation in the natural attenuation process.^{107,109,110} Similarly, some ENMs could be utilized to treat concentrated contaminants at source zones (*e.g.*, by enhancing ISCO or contaminant reduction), followed by biodegradation of the residuals (Fig. 5a). The initial high contaminant concentration increases the efficiency of using ENMs, because the desired reactions are favored at high concentrations. This process can also transform contaminants into less toxic forms that are readily biodegradable.^{111,112} Integration of nano- and bioremediation tools may broaden the choice of degradable contaminants, because some microorganisms can render alternative degradation pathways and produce more benign end products than abiotic treatments alone (*e.g.*, nitrate re-

duction to N₂ rather than NH₄⁺ achieved *via* an abiotic process, or complete triazine or RDX mineralization rather than abiotic reduction to nitroso intermediates).¹¹³ This is a desirable trait for remediating sites containing mixed contaminants. For example, fast initial removal of 1,1,2-trichloroethane by NZVI can relieve organochlorine respiring bacteria from the toxicity of this compound and stimulate bacterial degradation of 1,2-dichloroethane, which NZVI is typically unable to degrade.¹¹⁴

ENMs can also promote indirect degradation of contaminants by “boosting” microbial activity (Fig. 5a). Nutrients and genetic materials may be delivered using ENMs to stimulate native microorganisms that are capable of contaminant degradation. For example, oxygen-releasing ENMs, such as nanoparticulate calcium peroxide, can overcome groundwater dissolved oxygen limitations for biodegradation of contaminants driven by heterotrophs while generating ROS through Fenton's reaction for ISCO.^{115,116} Iron-containing nanoparticles can stimulate microbial production of biosurfactants that increase the solubility of organic contaminants.^{117,118} Microorganisms with the ability to transfer electrons extracellularly to iron oxides play an essential role in bioremediation of soils polluted with petroleum hydrocarbons.¹¹⁹ Both carbon-based and metal-based ENMs can be designed to serve as electron acceptors or electron shuttles and can improve interspecies and microorganism-contaminant electron transfer^{120–122} to promote biodegradation. For subsurface remediation, we should look beyond ENMs solely as an electron delivery device and instead as a tool to manipulate *in situ* microbial communities (Fig. 5a) and favor contaminant degradation; such as reducing

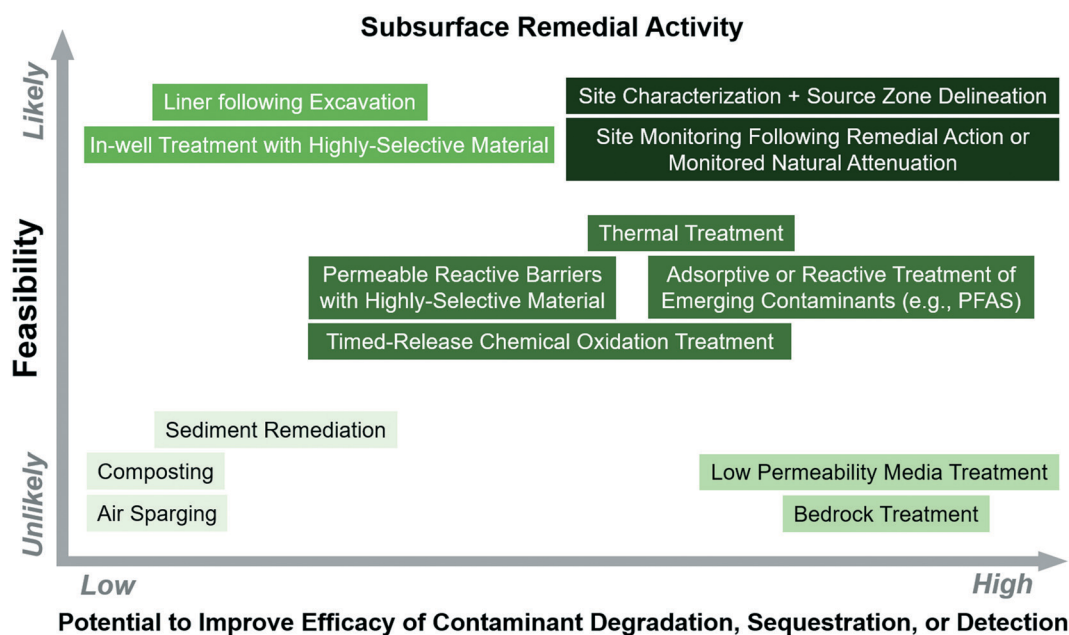


Fig. 4 Schematic showing the feasibility of using ENMs to improve selected remediation technologies vs. their potential to improve the efficacy of those approaches. The upper right quadrant (high feasibility and high impact) represent the most promising opportunities for ENMs. Box color roughly reflects the potential level of impact on each subsurface remediation approach, from low (lightest color) to high (darkest color).

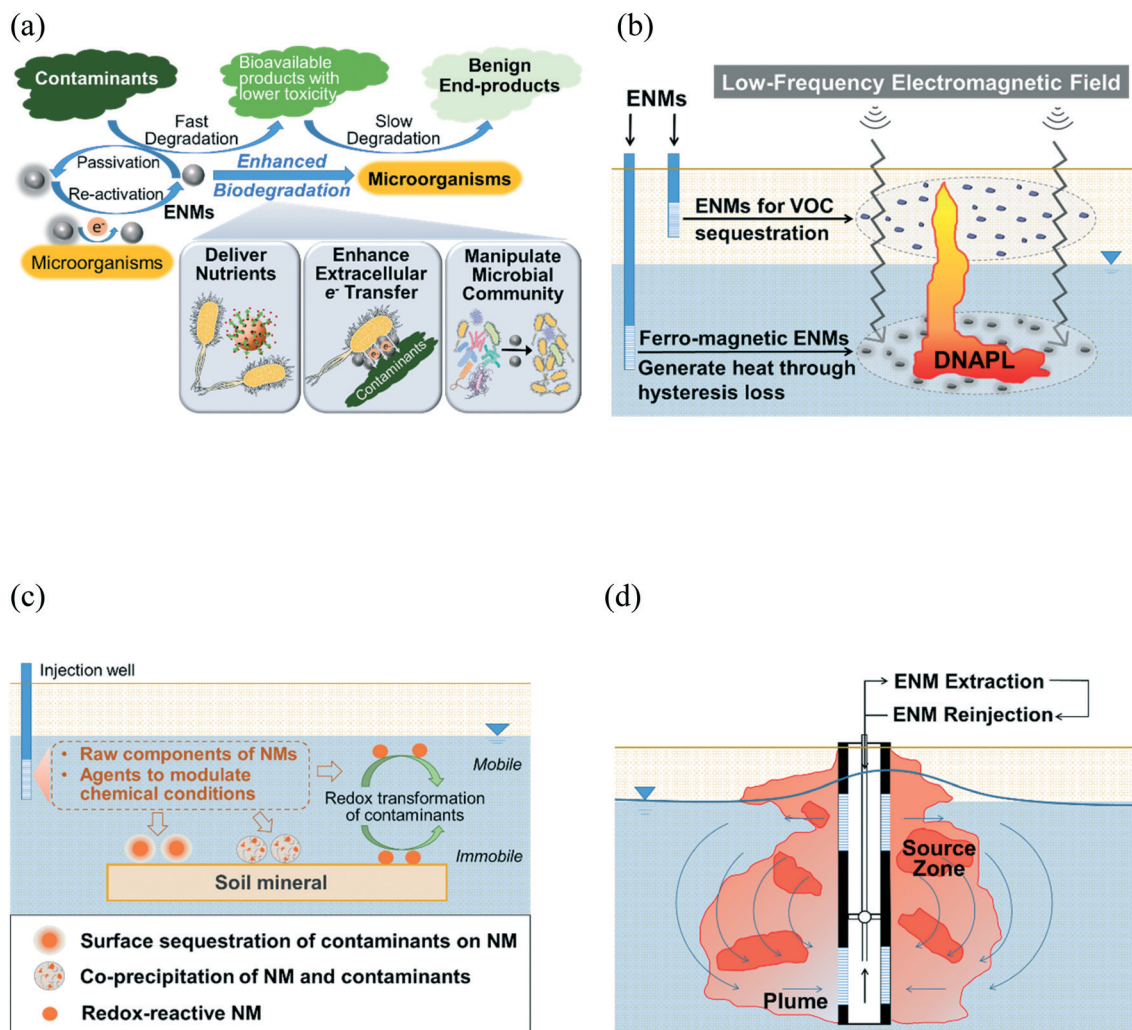


Fig. 5 Opportunities for nanotechnology to complement or to improve existing remediation technologies: (a) ENMs can be used to enhance the rates and performance of biodegradation approaches; (b) ENMs can enhance the performance of *in situ* thermal treatment and lower energy requirements; (c) *in situ* generation of nanomaterials (NMs) may be used to provide NMs in low conductivity regions to sequester or degrade contaminants; (d) groundwater circulating wells might be used to emplace ENMs over larger treatment areas compared to existing injection approaches.

microbial diversity without decreasing overall biodegradation capacity.^{123,124} For example, slow-releasing nanocapsules containing chemical stimuli for pollutant-degrading bacteria can be used to induce chemotaxis to selectively attract microorganisms to the source zones for efficient degradation of pollutants of interest. ENMs may also facilitate delivering signaling molecules (*e.g.*, autoinducers) to “tailor” the microbial population by taking advantage of quorum sensing.¹²⁵

NZVI serves as a good example of how ENMs synergistically work with bioremediation.^{40,126} During reductive treatment with NZVI, water-derived cathodic hydrogen can stimulate anaerobic bioremediation processes, such as reductive dechlorination.^{127–129} Specific bacteria act as electron shuttles to transfer electrons from NZVI *via* H₂ to the target contaminants, and thus exploit cathodic depolarization and contaminant degradation as metabolic niches. Furthermore, dissimilatory iron-reducing bacteria can also reactivate the

iron surface that gets passivated by oxides to improve the mass transfer of contaminants to surface reactive sites and form surface-associated Fe(II) to replenish abiotic reduction capacity.¹³⁰

Nano-enhanced thermal treatment

Thermal processes have been proven highly effective for rapidly treating organic pollutants *in situ*. Conventional thermal processes involve steam injection, electrical resistant heating, or natural gas addition and combustion.^{29,131–133} These treatments are often applied in low permeability zones, where other technologies requiring delivery of amendments are not feasible; however, the trade-off between rapid treatment potential offered by thermal processes and the high capital and energy requirements for these technologies may limit their application.

The unique electromagnetic hysteresis property of ferromagnetic ENMs (Fe, Ni, Cr, Sb, and various alloys) can provide thermally-enhanced *in situ* remediation of chlorinated VOCs (Fig. 5b). For example, NZVI delivered into an aquifer can generate heat through hysteresis loss under an applied electromagnetic field (EMF). Temperatures as high as 90 °C have been achieved in a laboratory feasibility study.¹³⁴ This enhances thermal dissolution from DNAPL source zones, desorption from VOC-sorbed soil, or volatilization from the vadose zone. The enhanced dissolution of VOCs plus enhanced reductive dechlorination by the NZVI increase degradation of tetrachloroethene (PCE) by ~60 fold compared to NZVI without EMF.¹³⁴ NZVI mixed into surfactant foams can be used to deliver these ENMs into the unsaturated (vadose) zone, whereupon EMF irradiation can generate heat (temperatures up to 100 °C) and lead to a TCE volatilization flux that is 40 times greater than the process without using EMF.^{135,136} This provides a new opportunity for thermal treatment in the vadose zone where ERH is not typically applied. This enhancement could also be achieved in DNAPL source areas where ERH is traditionally applied, *e.g.* clay lenses. However, this will require new methods to deliver the ENMs to those source zones as discussed later. Note that NZVI enables the use of low frequency EMF (LF-EMF) for heating. This provides significant energy savings compared to alternative approaches such as radio frequency induced heating without NZVI.

Nano-enabled LF-EMF approaches can also have other benefits. Preliminary research suggests that LF-EMF accelerates H₂ production from NZVI and helps in flushing out NAPL sources as an alternative NAPL recovery technique.¹³⁷ As discussed above, H₂ can be further used for enhanced anaerobic bioremediation. For more sophisticated thermal- and bio-enhanced *in situ* remediation, core-shell nanomaterials (polymer/metal nanoparticles) could be designed to release nutrients during the magnetic induction heating and thus further promote rapid down-gradient biodegradation of VOCs in plumes.

Carbon-based nanomaterials alongside with EMF inputs can also enhance treatment of petroleum hydrocarbon-contaminated sites. The unique dielectric properties of carbon, iron carbide, or other ENMs allow these to become superheated within the microwave field. For example, long chain (C12–C14) total petroleum hydrocarbons (TPH) above 1 wt% in soils (due to spills, tank/pipe leakages, *etc.*) weather slowly, and are only poorly biodegradable, which require remediation to meet “beneficial use” requirements. Upon addition of graphene to TPH contaminated soil, subsequent microwave irradiation could remove >90% of the TPH within minutes.¹⁰¹ The soil temperature rapidly increased to >100 °C and TPH is presumed to be removed by volatilization. Iron nanoparticles have recently been functionalized to selectively bind and detect hydrocarbons in the subsurface,¹⁰⁵ and could be a first step prior to external ENM activation and initiation of hydrocarbon removal. Longer-duration microwave exposure led to ignition of the soil, suggesting that microwave irradiation of ENM-amended soil can be used to initiate controlled smoldering, a reliable *in situ* or *ex situ* treatment

process to remove TPH.^{101,138} Carbon nanotubes (CNTs), graphene, carbon nanofibers, and other carbon materials show different thermal heating profiles. CNTs added to water containing organic pollutants rapidly degraded these pollutants upon microwave irradiation, likely because high temperatures (>1000 °C) localized at the ENM surface formed hydroxyl radicals that oxidized the pollutants. The materials remained stable over numerous microwave treatment cycles, suggesting that the carbon materials can be reused.¹³⁹

In situ synthesis of nanomaterials in low *K* zones

Migration of contaminants in subsurface environments is largely affected by heterogeneity. A greater mass of contaminants may reside in high hydraulic conductivity (high *K*) zones. However, residual organic and inorganic pollutants, trapped in low hydraulic conductivity (low *K*) zones in the subsurface environment (*e.g.*, clay lenses), serve as a continuous source of groundwater contamination. These low *K* source areas are notoriously difficult to treat, because it is difficult to deliver reagents into these areas, especially when they are surrounded by higher conductivity regions. For ENMs (which are solid particles), despite their small sizes, mixing effectiveness and mass transfer can be extremely limited in the low *K* areas due to interaction with the lithology of the saturated zone. Nevertheless, it may be possible to overcome the challenge of ENM delivery by synthesizing reactive nanomaterials *in situ* (Fig. 5c).

At environmentally relevant conditions (*e.g.*, at near neutral pH), dissolved metals, such as iron and manganese, can spontaneously transform into particulate metal oxides through hydrolysis reactions¹⁴⁰ or into particulate metal sulfides when reacting with dissolved sulfide in anaerobic environments.^{141,142} In the presence of macromolecules, such as natural organic matter, these mineral particles can be stabilized at the nano-scale,^{143,144} and can be reactive toward a variety of chemicals. For example, iron nanocrystals, such as mackinawite,¹⁴⁵ pyrite,^{146,147} hematite,¹⁴⁸ and magnetite^{149,150} have been demonstrated to strongly adsorb and/or reduce organic and inorganic contaminants, and therefore have great potential for *in situ* remediation. In addition to adsorption and reduction, another common practice of remediating heavy metal and metalloid contamination is to sequester the dissolved ions and complexes to solid phase through precipitation. For instance, NZVI is an effective ENM for chromium remediation because NZVI not only reduces Cr(vi) to Cr(III), but also generates Fe(III) to co-precipitate with Cr(III) *via* hydrolysis reactions.^{151,152} Both heavy metal and metalloid contaminants, such as Cu, Pb, Cr, and As, can co-precipitate with Fe to form nanocrystals.^{153–155} Indeed, *in situ* precipitation of Fe(II) and S(II) can form iron-sulfide coating onto quartz sands with little decrease in porosity, and this system can efficiently sequester As(III) from groundwater *via* both adsorption and precipitation.¹⁵⁵

The premise of *in situ* formation of nanomaterials for site remediation is largely dependent on the effective delivery of

raw components and manipulation of the geochemical conditions to prevent formation of nanoparticles in undesired locations. Precipitation occurs through homogeneous and heterogeneous pathways in natural aquatic environments. Nanoparticles generated through heterogeneous precipitation are immobilized on mineral surfaces, while homogeneous precipitation occurs in the aqueous phase and results in nanoparticles with greater mobility. The relative dominance of the two precipitation pathways is determined and thus can be modulated by groundwater chemistry as well as by the surface chemistry of the minerals.^{153,156} Laboratory and pilot scale studies are needed to determine the delivery methods and geochemical conditions that allow *in situ* emplacement of reactive nanomaterials.

Enduring challenges and future perspectives

As discussed above, there are many opportunities to leverage advances in nanotechnology for *in situ* (as well as *ex situ*) remediation. However, there remains significant challenges to their effective and sustainable use. Any innovation at the nano-scale for subsurface remediation must consider barriers to ENM transport and distribution in porous media.

Poor mixing and distribution of injected reagents and the diffuse nature of the subsurface target contaminant remain a well-known barrier for *in situ* remediation technologies. This is because groundwater flow is typically laminar in unconsolidated media, and transverse mixing of injected materials is minimal.¹⁵⁷ This problem is potentially more detrimental for ENM delivery due to their low diffusion coefficients compared to soluble reagents and their tendency to agglomerate.^{158,159} These challenges have generally limited the effective delivery distance of ENMs to a few meters using typical doses (of 5 to 20 g L⁻¹)^{160,161} and injection strategies (*e.g.*, pneumatic fracturing, hydraulic fracturing, gravity feed, and direct injection by Geoprobe). Therefore, new approaches to delivering ENMs *in situ* need to be developed and tested.

Groundwater circulating well (GCW) technology presents an underexplored opportunity for improved delivery/emplacement control of ENMs (Fig. 5d). GCW is an *in situ* treatment process for remediating aquifers contaminated with volatile hydrocarbons.^{161,162} A common embodiment of a GCW consists of a well, through which groundwater is extracted from the bottom *via* a screen with an in-well circulation pump, and is reinjected into the aquifer through another screen located higher up in the aquifer. This creates a circulating flow region within the capture zone surrounding the well. LNAPL, DNAPL, and dissolved organics within the capture zone can be removed by stripping within the GCWs.

There is potential to use GCW's to deliver ENMs that sequester and immobilize contaminants, or to locate and detect or encapsulate NAPL. ENMs and GCWs could be used in combination to create large *in situ* reactive zones for groundwater treatment. The advantage of this approach over the injection methods currently used is that the injected concentra-

tion of ENMs can be kept low to maximize the infiltration rate of the particles. For example, a 10 mg L⁻¹ ENM slurry with a flow rate of ~4 L min⁻¹ can theoretically deliver and emplace 3 kg of ENM in a 10 m³ region in about 50 days. This approach also has the advantage of being able to deliver reactive ENMs at a low rate into a source zone without unwanted impacts on the local hydrogeology that can arise from injection of higher concentration ENM slurries. To be effective, the physical structure and surface chemistry of ENMs need to be carefully controlled to minimize aggregation and straining by the aquifer medium for maximum penetration into the contaminated regions. Methods to target ENMs to entrapped DNAPL have been demonstrated in the laboratory.¹⁶³ Aquifer pretreatment, *e.g.*, polymer flushing, may also enhance delivery by decreasing attachment to the aquifer media surfaces and decrease straining.¹⁶⁴ There is a need to identify the optimal ENM properties and GCW operating conditions under field conditions.

Other challenges of applying ENMs for subsurface remediation include materials cost, sustainability, readiness and safety issues related to handling ENMs, and technology acceptance adoption. Currently, ENMs can cost more than the traditional remediation reagents. However, if small ENM quantities enable treatment where no other options exist, or can significantly shorten the time to achieve remediation targets, then there is an economic incentive to adoption. Additional methods to lower costs associated with ENM use must be explored, including increasing the number of well-publicized early successes that motivate demand and enhance the economy of scales, avoiding the need for high purity materials (making ENMs is inexpensive, separating and purifying them is expensive), identifying methods to reuse ENMs (*e.g.* by immobilizing them in reactors for above ground use in pump and treat scenarios), using only small amounts of ENMs to improve the performance of existing remediation technologies, and increasing selectivity to enhance transformation capacity and decrease amounts of ENMs required for treatment. It should be noted that the cost of “reagents” for a remediation project is rarely the dominant contributor of the overall cost. This is likely to be true for ENM-based remediation strategies as well. Monitoring costs are often the most significant, so remediating and closing a site faster can ultimately provide cost savings even in the “reagents” cost more.⁶⁹ A greater number of pilot scale studies can provide the cost and performance data needed to make this determination.

In situ remediation using NZVI has largely been accepted by regulators across the globe, in part because iron is a by-product which is already naturally occurring in groundwater. Many other engineered nanomaterials have relatively low risk to drinking water supplies.¹⁶⁵ Use of less abundant metals in ENMs may pose perception or regulatory barriers. In addition, uncertainty about the potential impacts of ENMs on human health and ecosystems that must be addressed.^{166,167} These problems should be addressable with early and continuous stakeholder engagement, and by deploying “safe by

design” approaches for ENMs that can manage the tradeoffs between high reactivity and greater toxicity potential. Similar challenges exist in the use of advanced materials for human medicinal applications,¹⁶⁸ and as such there has been a move toward porous nano-SiO₂, nano-cellulose, and liposomes in foods¹⁶⁹ and medicine¹⁷⁰ as delivery devices or additives. Liposomes can effectively deliver hydrophobic packages within nanoparticles with polar surfaces, and similar concepts could be applied in subsurface remediation – although few reports exist.

Sustainability of remediation approaches is an important consideration.¹⁷¹ Therefore, methods to synthesize ENMs, deliver these to the site (or synthesize on site), and form these *in situ* in an efficient way, continue to be pursued. Benefit-cost assessments, such as life cycle techno-economic analysis for ENM-enabled remediation should be performed for proposed ENM-enabled solutions, including consideration of ENM exposure risks.¹⁷² Finally, effective technology adoption strategies must be developed. Techno-economic analysis is one tool to promote technology adoption once the required data are available (*e.g.* economy of scale, achievable selectivity, *etc.*), but broad stakeholder engagement and well-monitored pilot scale testing will be required to gain broader stakeholder acceptance (including site owners, regulators, and the public) of these new technologies for *in situ* remediation. Pilot-scale field-testing is needed to demonstrate the long-term efficacy of proposed ENM-enabled remediation approaches; *e.g.*, to ensure that contaminants are completely degraded or that they remain sequestered for long times and to identify any unwanted impacts from the treatment. Researchers, practitioners, regulators, and all stakeholders need to participate in technology development to create a situation of “technology pull” into the market to solve real-world problems, as opposed to a “technology push” scenario where creators of a technology may overstate its benefits or apply it in a non-ideal setting to help diffuse the technology into the market.

Despite these challenges, nano-enabled remediation technologies will ultimately provide approaches for a broad range of legacy and emerging environmental contaminants, and can potentially provide novel solutions where no alternatives currently exist. The potential to synthesize ENMs with novel and multifunctional properties, and to use them in unique capacities, or to enhance existing remediation tools, make these highly valuable in the groundwater remediation tool kit. These technologies should continue to be developed and tested to discern “hype” from feasible opportunities and determine realistic performance expectations for *in situ* remediation technologies.

List of acronyms

AOPs	Advanced oxidation processes
BPA	Bisphenol A
BTEX	Benzene, toluene, ethylbenzene, and xylene
CNTs	Carbon nanotubes

DNAPL	Dense non-aqueous phase liquid
EMF	Electromagnetic field
ENMs	Engineered nanomaterials
EOR	Enhanced oil recovery
ERT	Electrical resistivity tomography
GCWs	Groundwater circulating walls
High <i>K</i>	High hydraulic conductivity
ISCO	<i>In situ</i> chemical oxidation
LF-EMF	Low frequency electromagnetic field
LNAPL	Light non-aqueous phase liquid
Low <i>K</i>	Low hydraulic conductivity
MIP	Molecularly imprinted polymer
MNA	Monitored natural attenuation
MOFs	Metal-organic frameworks
NAPL	Non-aqueous phase liquid
NZVI	Nanoscale zero-valent iron
PAHs	Polycyclic aromatic hydrocarbons
PCE	Tetrachloroethene
PFASs	Per- and poly-fluoroalkyl substances
PRB	Permeable reactive barrier
R&D	Research and development
TCE	Trichloroethene
TPH	Total petroleum hydrocarbons
VOCs	Volatile organic compounds

Conflicts of interest

There are no conflicts to declare.

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