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In situ nanoremediation of soils and groundwaters from the nanoparticle's standpoint: A review

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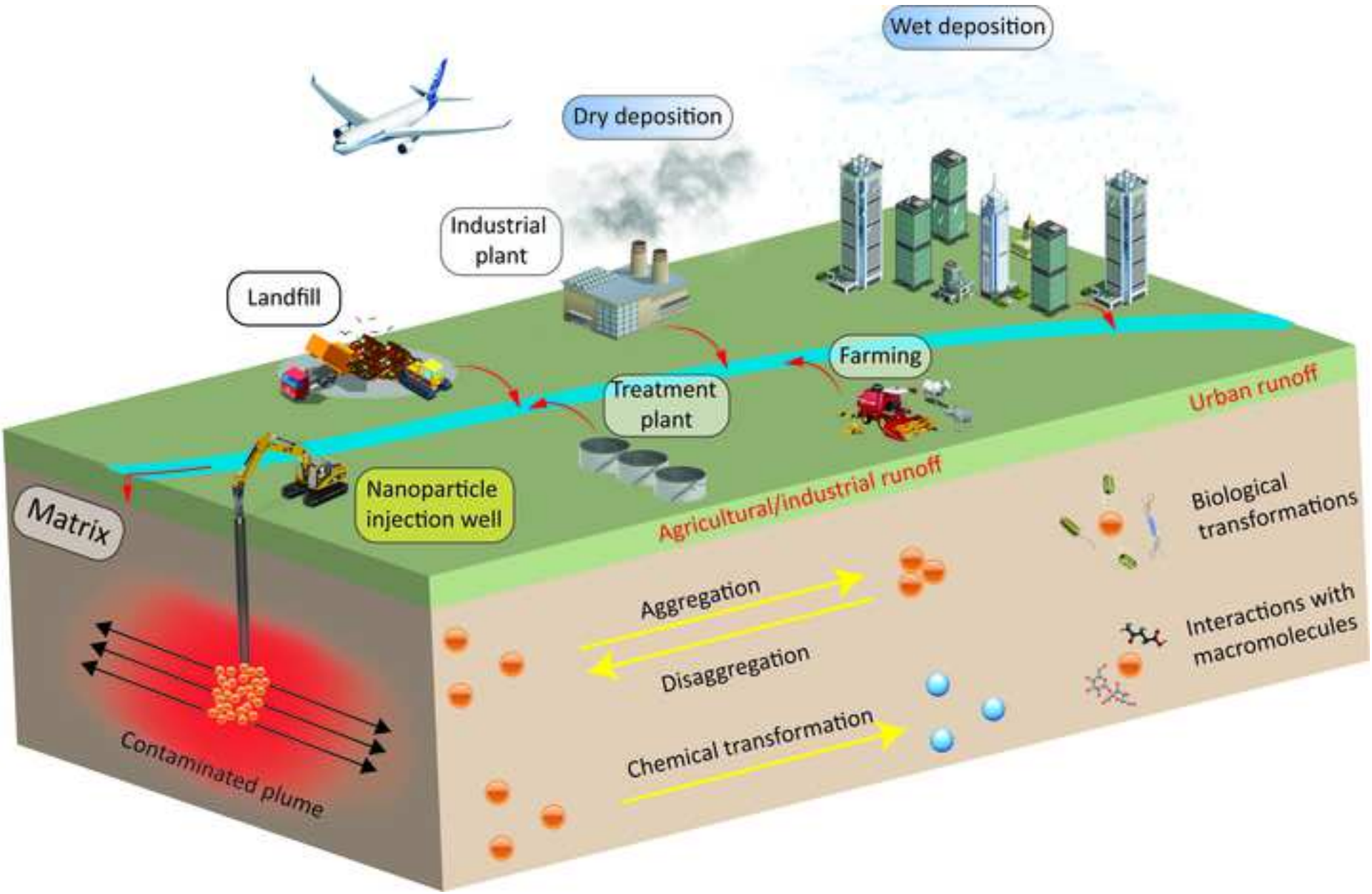
Graphical Abstract



Highlights (for review : 3 to 5 bullet points (maximum 85 characters including spaces per bullet point)

Highlights

- Anthropogenic pollution has continuously increased since the industrial revolution.
- Nanoparticles can provide solutions to *in situ* cleanup challenges.
- Nano-objects are increasingly being deployed in the field since the 2000s.
- Their use is not exempt of limitations (aggregation, human health risks).
- Their slow development in Europe is also due to economic motives and regulatory issues.
- Questions concerning toxicity and migration into the matrices need to be answered.

Manuscript (double-spaced and continuously LINE and PAGE numbered)
Click here to view linked References
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Abstract

Anthropogenic pollution coming from industrial processes, agricultural practices and consumer products, results in the release of toxic substances into rural and urban environments. Once released, these chemicals migrate through the atmosphere and water, and often find their way into matrices such as sediments and groundwaters, thus making large areas unsafe and potentially uninhabitable. Common pollutants, including heavy metals, metalloids, radionuclides, aliphatic hydrocarbons and halogenated organics, are known to adversely affect physiological systems in animal species.

Pollution can be cleaned up (one could also say "remediated") using a range of techniques such as coagulation, reverse osmosis, electrochemistry, oxidation and biological methods, amongst others. The use of nanoparticles (NPs) extends the range of available remediation technologies and offers particular benefits, not only by degrading, transforming and/or immobilizing contaminants, but also by reaching inaccessible areas and promoting biotic degradation. The development of NPs is understandably heralded as an environmentally beneficial technology; however, it is only now that the ecological risks associated with their use are being evaluated.

This review presents recent developments in the use of engineered NPs for the *in situ* (*i.e.* direct delivery into contaminated sites) environmental remediation of two paramount environmental matrices: soils and groundwaters. Emphasis will be placed on (i) the successful applications of nano-objects for environmental cleanup, (ii) the potential safety implications caused by the challenging requirements of [high reactivity toward pollutants] *vs.* [none reactivity toward biota], with a

thorough view on their transport and evolution in the matrix, and (iii) the perspectives on scientific and regulatory challenges.

Keywords: Remediation; ecotoxicity; nano-oxides; nanoscale zero-valent iron; multimodal character

1. Introduction

Since industrialization in the 1940s and 1950s, developed and developing societies continuously emit massive amounts of organic and inorganic pollutants – such as heavy metals, persistent organic pollutants, plastics, pesticides, personal care products and pharmaceuticals – into air, waters and soils. As a result, the nature and distribution of contaminants in the environment has changed in recent history (Doyle et al., 2020; Rasheed et al., 2019; Sauvé and Desrosiers, 2014; Tarr, 2002).

Increase in pollution of surface waters and groundwaters from a wide variety of industrial, municipal and agricultural sources, has seriously altered water quality, thus reducing the supply of freshwater for human consumption and development. According to a 2011 Food and Agriculture Organization of the United Nations report, 25 % of the global soils were highly degraded and 44 % significantly degraded (Food and Agriculture Organization of the United Nations, 2011). During the last hundred years, the number of landfills, military installations, oil fields, private properties, manufacturing and industrial contaminated sites, has been increasing globally while many man-made chemicals such as polychlorinated biphenyls (PCBs) or dichlorodiphenyltrichloroethane (DDT) do not degrade for hundreds of years and can migrate in the sediments and in living organisms following the food chain (Sijm et al., 2007). Thus, human populations continue to be exposed to PCBs despite their ban in the US since 1979, inducing human health consequences including reproductive dysfunction, neurobehavioral deficiencies and increased cancer risks (Davis, 2002). Polycyclic aromatic hydrocarbons (PAHs) form another important family of contaminants that occur naturally in coal, gasoline and crude oil or as combustion byproducts. PAHs are ubiquitous in the environment and are probable human carcinogens, not to mention their connection with many respiratory medical conditions (Alegbeleye et al., 2017; Idowu et al., 2019).

Equally important are chlorinated organic compounds (COCs) ranking among the most persistent environmental pollutants. These chemicals are applied to a variety of applications, including their use as solvents, pesticides, degreasing agents, biocides, pharmaceuticals, plasticizers, hydraulic and heat transfer fluids, intermediates for chemical synthesis, and numerous other industrial functions. Their large-scale use in industry and agriculture has induced a substantial entry of these chemicals into all major environmental compartments (*i.e.* soils, sediments, water and air). Due to the persistence and potential toxicity of different organohalides, in addition to their propensity to bioaccumulate in the food chain, amongst other adverse effects, extensive efforts have been made to replace halogenated chemicals today (Häggblom and Bossert, 2004).

Reference should also be made to heavy metals, whose multiple industrial, domestic, agricultural, medical and technological applications have led to their wide distribution in the environment (Masindi and Muedi, 2018). Consequently, human exposure to heavy metals has risen dramatically, raising concerns over their potential effects on human health and the environment. Metals such as arsenic, lead, cadmium, nickel, mercury, chromium, cobalt, zinc and selenium are highly toxic, even in minor concentrations, when they accumulate in the body and food chain.

In this context, the global market for environmental remediation technologies was valued at about $65.2 billion in 2016 and is expected to expand to $82.7 billion in 2022 (Boots, B, 2017). The US Environmental Protection Agency (EPA) prioritized in 2004 the cleanup of more than 900 sites in the US alone (United States Environmental Protection Agency, 2007). Similarly, the European

Environment Agency (EEA) estimated seven years later that 3 million areas in the European Economic Area were potentially contaminated sites, of which nearly 250,000 need to be urgently remediated (European Environment Agency, 2014). Since then, anthropogenic pollution has continuously increased, thus endangering human health and wildlife. Despite the 2001 Stockholm Convention on Persistent Organic Pollutants, it has been repeatedly reported that industrialized countries forming the contracting parties are not making adequate efforts to remediate contaminated areas (Law and Jepson, 2017).

In response to these challenges, various environmental remediation techniques aim at removing and/or degrading contaminants especially in polluted soils, surface waters and groundwaters as well as in sediments. Some of them, known as *ex situ* techniques, involve excavating the matrix to be remediated from the polluted sites and then treating the pollution aboveground. These methods are highly energy-intensive and costly, considerably disruptive to site operations and face challenges to meet permissible remediation standards. Another limitation is that they may leave concentrated and hazardous waste residues, which require further disposal (Koul and Taak, 2018; Kuppusamy et al., 2016a).

By contrast, other techniques clean up the contamination while it is still on site. These *in situ* remediation techniques exploit biological, chemical or physical processes, and are being increasingly used to avoid excavation and transport of contaminated materials. While effective in some cases, conventional *in situ* remediation technologies have shown a limited capacity to remove pollutants, more specifically during massive cleanups. Other limitations are: time-consuming processes, high production of sewage sludge, generation of toxic by-products and, in some cases, a detrimental impact on matrix geochemistry and biota (Gomes et al., 2013; Kuppusamy et al., 2016b). These methods could be slowly phased out over the coming decades with the arrival of rapid, inexpensive and efficient nanoremediation approaches (Patil et al., 2016; Zhu et al., 2019).

Indeed, there is strong evidence that nanoparticles (NPs) could provide solutions to environmental challenges by being injected into the matrix and subsequently by degrading and/or immobilizing contaminants (Bardos et al., 2018). The reduced size of NPs increases both the number of sites susceptible to adsorb or react with pollutants, theoretically improving the degradation kinetics, and their ability to migrate farther or deeper in soil and groundwater than their macro-sized counterparts to chase pollutants. Even though the use of nano-objects for environmental remediation is still in its infancy, it is increasingly being deployed in the field.

In recent years, nanomaterials as diverse as nanoscale zero-valent iron (nZVI) – which represents the majority of field-applications –, carbon nanotubes and nano-oxides have been applied for the remediation of a variety of contaminants including chlorinated compounds, aromatic hydrocarbons and heavy metals (Ingle, A.P. et al., 2014). By 2009, nanoremediation had been successfully applied and documented in more than 40 cleanup sites, including United States, China, North and South Korea, Japan, Hong-Kong and Canada (Karn et al., 2009). In 2011, a report commissioned by the Department for Food the Environment and Rural Affairs (U.K. Government) identified 58 deployments of nZVI in the field, from pilot tests to commercial applications (Bardos et al., 2011). By the end of 2016, this listing was expanded to approximately 100 field-based deployments (Bardos et al., 2018). In addition, Karn et al. showed that media treated with NPs in field applications were predominantly groundwater (60 %), combinations of soil and groundwater (16 %) and soils alone (2 %), hence our choice to focus this review on soil and groundwater contamination (Karn et al., 2009).

If most applications have been limited to the treatment of groundwater and wastewater, extensive research is led to treat soils, sediments and even gases, while developing other promising nanomaterials toward an extended range of treatable contaminants. Besides nZVI, nanoscale materials such as bimetallic nanoparticles, metal oxides, nanogoethite and titanium dioxide have been explored. In this search, the ideal nanoparticle is expected to be highly reactive and detoxify

pollutants locally without impacting the matrix biota, while being ultimately transformed into an innocuous material (Phan and Haes, 2019).

Furthermore, nanotechnology has the potential to bring down the cost of remediation. In 2003, US EPA, together with the oil company BP, checked if bimetallic nanoparticles (BNP) – in this case nZVI coated with Pd – were able to reduce 1,1,1-trichloroethane in an arctic environment located in Alaska. Cost comparison was done between this method and a "traditional" excavation method, in which a portion of the soil is removed, treated offsite and replaced, or simply incinerated. The BNP process was estimated to be up to seven times more cost effective than other remediation alternatives previously evaluated (Kuiken, 2010). This trend was confirmed by a study conducted by PARS Environmental Inc. who reported cost savings of 80-90 % when using nZVI in comparison with pump-and-treat methods and permeable reactive barrier technologies to clean up trichloroethylene (PARS Environmental Inc, 2004). In addition to the potential cost savings, the time frame for site cleanup through nanoremediation is significantly reduced from months to days.

However, the use of nanomaterials is not exempt of limitations such as a propensity for fast passivation, easy aggregation, susceptibility to geochemical fluctuations, potential environmental and human health risks (Zhu et al., 2019). As a matter of fact, risks regarding the adverse effects that nZVI and other NPs could have on indigenous microbial communities and ecosystem functioning at different stages of the remediation process are poorly understood and documented, leading to precautionary and conservative regulatory positions (Bardos et al., 2018). This review examines the progress made since the early 2000's in nanoremediation research and developments from laboratory testing to pilot- and field-scale applications. Sections 2 and 3 aim at providing a general background to detail the main groups of target pollutants and the existing *in situ* technologies conventionally used. With the aim of designing NPs suitable for remediation, section 4 focuses on the different mechanisms of action exhibited by nanoremediators to clean contaminated soil and groundwater (referred to as matrices). The properties of the main types of nanomaterials are described with an emphasis on nanoscale zero-valent iron (nZVI) and nano-oxides. Additionally, we summarize important aspects of pilot- and field-scale applications from existing literature and substantiated reports. Indeed, if laboratorial studies are relevant to expand the understanding of the NPs efficiency and their transport in the media subjected to treatment in a small and controlled scale, pilot- and full-scale studies from field applications legitimately constitute the primary goals of nanoremediation. The fate of nanoparticles in the environment, *i.e.* their transport, distribution and evolution in soil and groundwater, is discussed in section 5. The dynamic interaction between particle and environmental matrices is described prior to reviewing the main results of nZVI field applications. Section 6 summarizes the state of knowledge on the ecotoxicity of the main nanoremediators, including their impact on microbiota (bacteria and fungi) and higher organisms. Section 7 critically considers the past, present and future of nanoremediation research from practical, environmental and regulatory perspectives. Finally, section 8 summarizes the state of the art along with the requirements which will probably drive the future of nanoremediation.

2. Main groups of contaminants

First of all, the difference between pollution and contamination must be clarified. According to P.M. Chapman: "Contamination is simply the presence of a substance where it should not be or at concentrations above background. Pollution is contamination that results in or can result in adverse biological effects to resident communities. All pollutants are contaminants, but not all contaminants are pollutants" (Chapman, 2007). Consequently, contaminants can be pollutants as soon as they have a detrimental effect on the environment. Also, pollutants can either be naturally occurring

contaminants or foreign elements such as chemical substances and forms of energy (light, noise or heat).

Contamination derived from natural sources like volcanic eruptions or forest fires tends to spread and to disappear in moderately short time (Hong et al., 1996). Alternatively, anthropogenic pollution started with wood fires, excrements and dust from mining. However, the industrial revolution of the mid-19th century introduced new sources of pollution. Modern anthropogenic pollution sources includes: (i) municipal wastewater – which carries detergents, organic matter and inorganic compounds present in everyday personal care products – and urban runoff that contains contaminants originating from tires and engines, (ii) wastewater from agriculture and livestock activities, including pesticides, fertilizers, hormones, antibiotics and other synthetic products, (iii) industrial wastewaters that vary in terms of composition and flow rate, and (iv) the release of toxic compounds, such as CO, O_3, NO_x, SO_x, and volatile organic compounds from vehicles and industrial activities (Trujillo-Reyes et al., 2014; Yuvaraj and Mahendran, 2020).

In industrialized societies, air may contain numerous pollutants such as carbon monoxide, chlorofluorocarbons, heavy metals and metalloids (As, Cr, Pb, Cd, Zn and Hg), hydrocarbons, nitrogen oxides, organic chemicals (volatile organic compounds known as VOCs and dioxins), sulfur dioxide and particulates. These compounds are then removed from the atmosphere in the form of wet deposition during rainfalls, thus infiltrating soils and surface waters. Emission of nitrogen and sulfur dioxide, mostly due to burning of oil, coal and gas, generates acid rains that infiltrate and contaminate soils. The most common chemicals involved in soil pollution are petroleum hydrocarbons, pesticides and heavy metals. Soil contamination can also happen as a result of underground storage tanks rupturing or the leaching of waste from landfills. Mining, fertilizer applications, oil and fuel dumping and a multitude of other environmental issues can also cause pollution of soils (Yuvaraj and Mahendran, 2020).

In parallel, groundwater is especially vulnerable because it constitutes the end-of-pipe matrix in areas where population density is high and human use of the land is intensive. Contaminants may reach groundwater from (i) stored industrial wastes, (ii) sources below the land surface but above the water table, such as septic systems or leaking underground petroleum storage systems, (iii) structures beneath the water table such as wells, or (iv) contaminated recharge water (United States Environmental Protection Agency, 2015). Also, a broad description of organic pollutants and their cleaning priorities was established during the Stockholm convention in 2001, aimed at protecting human health and the environment from persistent organic pollutants (Stockholm Convention Clearing House, 2001). Common contaminants of concern in soil and groundwaters are summarized in Table 1 (from organics to inorganics).

Table 1
Common contaminants of concern in soil and groundwaters.

Type of pollutant	Example	Source	Toxicity	Reference
Chlorinated organic compounds (COCs)	Trichloroethane, trichloroethylene (TCE), tetrachloroethene (PCE) and *p*-chloroaniline	Pesticides, industrial degreasing and manufacturing	Persistent to biotic degradation, accumulation tendency in the food chain, endocrine disruptor, carcinogenic	(Ramamoorthy and Ramamoorthy, 1997)
Polychlorinated biphenyls (PCBs) $C_{12}H_{10-x}Cl_x$	3,3',4,4'-Tetrachlorobiphenyl (PCB77) 2,3,3',4,4'-Pentachlorobiphenyl (PCB105)	Industrial and commercial applications including electrical and hydraulic equipments, plasticizers and pigments.	Cause cancer in animals and probable human carcinogens	(Hornbuckle and Robertson, 2010)
Petroleum hydrocarbons*	Diesel, kerosene, naphtha, Jet A	Mixture of distillates extracted from crude oil for use as propellant, lubrication additives and degreasers	Poisonous by ingestion, dermal irritation, risk of fire, possible carcinogens	(Khan et al., 2018)
Polycyclic aromatic hydrocarbons (PAHs)	Anthracene, fluorene, phenanthrene	Incomplete combustion of organics such as oil, coal and wood	Toxic, mutagenic and carcinogenic properties	(Kuppusamy et al., 2017)
Organic pollutants classified by the World Health Organization (WHO)	. Very Volatile Organic Compounds (propane, butane and methylchloride) . Volatile Organic Compounds (formaldehyde, toluene, acetone) . Semi Volatile Organic Compounds like pesticides (DDT, chlordane) and fire retardants (PCBs and their brominated counterparts PBBs).	Among the world's most widely occurring pollutants of subsurface soil and groundwater because of the pervasive production and use of organic solvents and hydrocarbon fuels	N/A**	(World Health Organization, 1989)
Nitroaromatic compounds (NACs) R-NO_2	Nitrobenzenes, nitrofluorenes, 3-nitrobenzanthrone	Explosives, pesticides and solvents	Potential carcinogens	(Kovacic and Somanathan, 2014)
Emerging contaminants (ECs)	Diclofenac, ibuprofen, bisphenol A, methylparaben, MDMA	Pharmaceuticals and personal care products, illicit drugs, surfactants and gasoline additives	Alter the endocrine system of humans and wildlife at low concentrations, accelerate the development of antimicrobial-resistant bacteria	(Petrie et al., 2015)
Phenols and anilines	Cresol, xylenol, 4-chloroaniline, 3,4-	Degradation of natural organic matter	Hematotoxic, genotoxic,	(Harvey et al.,

	dichloroaniline	present in water, synthetic dye industry, disposal of industrial/domestic wastes and agricultural runoffs.	hepatotoxic, mutagenic, carcinogenic	2002)
Aromatics known as BTEX	Benzene, toluene, ethylbenzene and xylene monomers	Petrochemical materials, used as intermediates in the synthesis of many consumer products, emissions from motor vehicles and aircraft exhaust	Potential endocrine disrupting properties, skin and sensory irritation, central nervous system-CNS problems, carcinogenic	(Bolden et al., 2015)
Heavy metals and metalloid contaminants	Hg, As, Cu, Pb and Cr among the most toxic	Mining and industrial wastes, agricultural activities, vehicle emissions, lead-acid batteries, fertilizers, paints and waste disposal	Toxicity and carcinogenicity, bioaccumulation in the food chain and persistence in the environment	(RoyChowdhury et al., 2018)
Oxyanions based on arsenic and selenium	. Arsenite As(III) (H_3AsO_3, $H_2AsO_3^-$, $HAsO_3^{2-}$) . Arsenate As(V) (H_3AsO_4, $H_2AsO_4^-$, $HAsO_4^{2-}$) . Selenate (SeO_4^{2-}) / selenite (SeO_3^{2-})	Naturally occurring in the environment, released from tunnel-excavated sedimentary rocks, processing of fossil fuels, irrigation of soils for crop production	Lethal and carcinogenic effects, accumulation in aquatic food webs	(Sun et al., 2014)
Radionuclides	^{137}Cs, ^{90}Sr, ^{99}Tc, ^{237}Np and U isotopes	Nuclear weapons testing, nuclear facility releases or radioactivity wastes	Carcinogenicity, radiotoxicity	(Skipperud and Salbu, 2018)
Nitrates and phosphates	NO_3^-, PO_4^{3-}	Drainage from farmlands (fertilizers, runoff from manure…), sewage effluents	Induce excessive inputs of nutrients and disrupt ecosystem balances	(Beiras, 2018)

*Petroleum Range Organics (PRO) include hydrocarbons from C_2 to C_5, Gasoline Range Organics (GRO) from C_6 to C_{10-12} and Diesel Range Organics (DRO) from C_{8-12} to C_{24-26}.
** The WHO classification covers a too wide spectrum of chemical substances. Additionally, there is no clear and internationally accepted definition of each sub-group.

3. Existing *in situ* technologies

The main approaches to remediation are known as *ex situ* and *in situ*. *Ex situ* implies the physical extraction of the contaminated matrix – soil excavation or groundwater pumping – followed by an off-site treatment. Inversely, *in situ* involves treating pollutants on-site. The main benefit of *in situ* techniques is that removal and transport of contaminated media is not required, thus considerably decreasing the associated costs. However, *ex situ* treatments are easier to monitor (Kuppusamy et al., 2016a), although they are relatively expensive and slow. Until 1992, the predominant treatment technology to specifically address groundwater contamination was the pump-and-treat technique (*i.e.* the extraction of groundwater from an aquifer and its treatment aboveground); yet the average pump-and-treat system operates for about 18 years. Meanwhile, public sites remediated by pump-and-treat operations in the U.S. have fallen to less than 20 % in 2005 (Karn et al., 2009). Consequently, *ex situ* remediation techniques are expected to be continuously phased out in the future for the benefit of *in situ* techniques. *In situ* environmental remediation can be achieved using three different approaches: physical, chemical, and/or biological (Ingle, A.P. et al., 2014)**.**

Physical remediation is the oldest method used for the treatment of soils, allowing for faster cleanups. For instance, soil washing involves the combination of solvents and mechanical processes to scrub soils and solubilize specific contaminants. This process separates coarse soil from fine soil, generally bound to hydrocarbon contaminants, and can also be associated with other methods such as incineration (Bradl and Xenidis, 2005).

Another example is the Soil Vapor Extraction (SVE) technique in which a vacuum is applied to the soil, usually through boreholes and trenches, to generate an air flow in the unsaturated zone soil and remove volatile and some semi-volatile contaminants. The extracted air containing the contaminants can then be processed to recover or destroy the contaminants. SVE remediation systems are often combined with other techniques such as air sparging for the additional treatment of saturated soils and groundwaters; pressurized air is injected into the matrix to enable the hydrocarbons to switch from dissolved to vapor state (Sabour et al., 2017).

Moreover, thermal treatments are specifically applied for the remediation of contaminated soils by making use of the different melting point of substances (Vidonish et al., 2016). Heat – generated into the subsurface by electrical resistances or radio frequencies – is used to convert the chemicals into gases, thereby increasing their mobility and making them extractable *via* collection wells. Pyrolysis and conventional incineration destroy the contaminants, while vitrification destroys or separates organics and immobilizes some inorganics (Taube et al., 2008). Thermal methods can be particularly useful for dense or light nonaqueous phase liquids (DNAPLs or LNAPLs) such as chlorinated solvents, PCBs, benzene and toluene. However, the main drawbacks of these treatments are high energy demand, decreased soil fertility and destruction of the remaining biota (Vidonish et al., 2016).

Chemical remediation implies the transformation of contaminants by added chemicals to a less toxic or more separable form. This efficient method is widespread although it requires periodical treatments and dedicated equipment. Chemical methods include actinide chelators, chemical immobilization, critical fluid extraction, oxidation, *in situ* catalyzed peroxide remediation and photodegradation (Polo et al., 2010). For example, chemical oxidation consists in injecting an oxidant (*e.g.* oxygen, ozone, hydrogen peroxide or hypochlorite) into the soil, generally in the saturated area, to activate the decomposition of organic components (Usman et al., 2018).

Finally, *bioremediation* is the use of microorganisms (*aka* bioremediators) to remove pollutants from soils, sediments, sludge or groundwaters, and transform them into innocuous (Vidali, 2001). Examples of such technologies are bioventing, bioleaching, land-farming, rhizofiltration and biostimulation. Plants and microorganisms like bacteria, fungi, yeasts and actinomycetes are used as bioremediators to detoxify a wide variety of pollutants, from polycyclic aromatic hydrocarbons (PAHs) to heavy metals (Shahsavari et al., 2019).

Choice of remediation technology is generally associated with the type and accessibility of contaminants, the characteristics of the soil or aquifer (density, permeability, heterogeneity and reactivity among others), the global approach (aggressive measures *vs*. long-term management *vs.* impact to biota), the drilling conditions and the cost/benefit ratio. A recent investigation has shown that coupling two common treatments – for instance *in situ* chemical oxidation (ISCO) and bioremediation – provides in many cases more efficient and extensive cleanup of contaminated subsurfaces, hence a current trend to associate technologies (Sutton et al., 2011).

The US EPA reported in 2007 that the selection of *in situ* treatments continuously increased and represented 18 % of the selected projects for groundwater treatments (*vs.* 90 % for pump-and-treat treatments). The most widely used technologies include air sparging (30 %), bioremediation (27 %), chemical treatments, permeable reactive barriers and multi-phase extraction (United States Environmental Protection Agency, 2007). Indeed, application of *in situ* bioremediation and chemical treatments in field conditions have also increased significantly in recent years as an alternative to excavation and *ex situ* treatments (Liu et al., 2020). However, as mentioned in Table 2, *in situ* remediation techniques suffer critical limitations, since they can affect the physical structure and biological activity of the treated soils by introducing aggressive chemicals or by generating toxic by-products (Trujillo-Reyes et al., 2014).

Table 2
Pros and cons of the most commonly used *in situ* technologies. Adapted from (Kuppusamy et al., 2016b).

Remediation approach	Technique	Advantages	Disadvantages
Physical	Thermal	• Quick cleanup times • Effective removal of DNAPL in soil and groundwater • More complete remediation of many recalcitrant pollutants • Useful in low permeability silts and clays • Dissolved and adsorbed pollutants reduced to low levels	• High system operating costs, especially electrical costs • More likely safety hazards • Potential off-site migration of pollutants • Necessary to establish hydraulic and pneumatic control of the site
	Soil Vapor Extraction	• Relatively short and inexpensive • Little risk of environmental release • Ease of installation • Well-known technique	• Contaminant volatilization limited by high concentrations of organic matter • Higher vacuums required for highly saturated soils • Applicable only for unsaturated soil and soils with high permeability • Residual liquids following off-gas treatments may require disposal
Chemical	Oxidation	• Fast • Variety of oxidants and activation approaches • Applicable to a wide range of	• Inappropriate for heavy metals, radionuclides, inorganic salts • Potential need for large amounts of chemicals

	subsurface conditions • Low mobilization costs	• Limited in low permeability soils and groundwater zones • Side effects toward biota and matrices (*e.g.* permeability reduction and gas evolution)
Biological	• Lower cost • Minimal exposure to humans • Minimal disruption of site • Faster than pump-and-treat • Breakdown to innocuous substances • Larger zone of treatment • Little secondary waste	• Potential incomplete transformation • Microorganisms potential sensitivity to toxins or highly concentrated contaminants • Intermediate product may be more toxic (*e.g.* TCE to vinyl chloride) • Some pollutants are recalcitrant (inorganics and some organics) • Longer term processes • Sensitive to some soil parameters (presence of humic materials, clay) • Difficult to treat low-permeability soils

It is of interest to mention the development in the early 1990s of permeable reactive barriers (PRB) for sustainable *in situ* remediation of groundwaters. The principle of PRB lies in the emplacement of a reactive medium in the subsurface designed to intercept a contaminant plume (Obiri-Nyarko et al., 2014). As the contamination plume passively migrates through the barrier under the influence of the natural hydraulic gradient, the contaminants react with the media leading either to their transformation to less harmful compounds or absorption and fixation to the remediation materials. The decontamination methods include: i) sorption and precipitation, ii) chemical transformation and iii) biodegradation. In a first field-scale operation published in 1998, a mixture of granular iron and sand immobilized into sealable-joint sheet piling was used for the degradation of trichloroethene and tetrachloroethene in a Canadian sand aquifer (O'Hannesin and Gillham, 1998). Thereafter, most of the published documents on PRBs have focused on barriers filled with zero valent iron (ZVI) as a reactive material directed against chlorinated solvents, even if their application was extended to other contaminants (halogenated aliphatic hydrocarbons, metals, metalloids, radionuclides, pesticides, petroleum hydrocarbons and nutrients) using microorganisms, activated carbon, zeolites, peat, saw dust and oxygen releasing compounds, amongst others. As the use of micro-sized materials has been well documented, it has been suggested that nanoparticles may also be suitable as the reactive component within the PRB matrix and, more generally, for *in situ* applications.

4. Nanoremediation

In recent years, the use of engineered nanoparticles (NPs), such as nanoscale zero-valent iron (nZVI), bimetallic particles and nano-oxides, has gained increasing amounts of attention. Nanoparticles flowing through pore spaces can also reach inaccessible areas such as crevices and aquifers, thus eliminating the necessity for costly traditional operations (Ingle, A.P. et al., 2014).

These remediation materials have three modes of action:

1) The *physical mode* involving the adsorption and immobilization of the contaminants onto the surface of the particles due to their large surface area and reactivity. For instance, iron oxide Fe_3O_4 particles (12 nm in diameter) were used to remove arsenic from water following sorption and magnetic separation (Yavuz et al., 2006).

2) The *detoxification mode* inducing and/or catalyzing the initial chemical breakdown leading to the transformation of toxic compounds to less harmful products. Oxidation-reduction reactions are the predominant mechanisms, as in the case of photocatalytic titanium oxide TiO_2 nanoparticles for the oxidation of organics (Abdelraheem et al., 2020), or nanoscale zero-valent iron (nZVI) for their reduction (Fajardo et al., 2019).

3) The *bio-cooperative mode* in which the particles assist biotic degradation by increasing bioavailability and degrading pollutants into more bioremediable species. As an example, Fe_3O_4 NPs were used as ion-providers to improve biogas production in anaerobic digestion processes (Casals et al., 2014). A recent review by Abdelsalam and Samer underlined that nanoparticles tend to biostimulate bacterial cells, thus enhancing bacterial activity and the kinetics of bacterial growth (Abdelsalam and Samer, 2019). The authors also pointed out that iron-based nanoparticles have been generally observed to enhance biogas and methane production. Two assumptions are generally put forward for this: the corrosion of iron oxide NPs is suspected to provide sufficient amounts of essential iron in the form of Fe^{2+} needed for the microbial proliferation; conductive (nano-Fe_3O_4) and semi-conductive (nano-Fe_2O_3) particles could serve as an electron donor to facilitate microbial interspecies electron transfer, a phenomenon known as electric syntrophy that boosts methanogenesis (Zhu et al., 2021).

The multimodal character of nanoremediators towards environmental pollutants is illustrated in Figure 1.

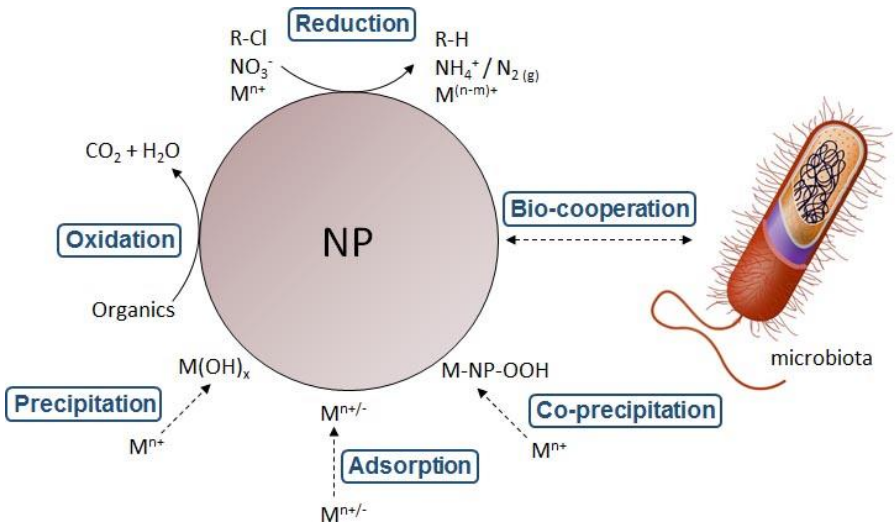

Fig. 1. Decontamination mechanisms mediated by nano-objects. M: metal; NP: nanoparticle. Adapted from (O'Carroll et al., 2013).

Due to this multimodal character and the plethora of nanostructures available, each category of contaminant may potentially find its remedy. Inorganic cations and anions, because of their charge, are prone to complexation and adsorption on the surface of metal oxide nanoparticles. Other strong adsorbents are carbon- and polymer-based NPs, as well as minerals exhibiting high surface areas (Kumari et al., 2019). Particularly interesting is the use of magnetite/maghemite (Fe_3O_4/Fe_2O_3) NPs as polar adsorbents, due to their ease of detection in the presence of magnetic fields. One could also use the magnetic properties of these iron-based NPs to facilitate the separation and recovery of adsorbates (*e.g.* heavy metals) and turn them into new resources, following the principles of circular economy (Gottardo et al., 2021; J. Zhang et al., 2020).

While the remediation of heavy metals predominantly relies on mere adsorption, remediation of redox active inorganic anions (particularly those present in high oxidation states) and radionuclides

(*e.g.* U(VI)-U(IV) and Tc(VII)-Tc(IV)) requires reducing conditions (Bodzek, 2013; Merkel and Hoyer, 2012). In this case, zero-valent metal NPs (Fe, Co, Ni, Cu) alone or covered by oxide layers, should be applied (Shanmugham et al., 2020). As an example, perchlorate anion ClO_4^- is a strong oxidizing agent (E^0=1.29V) and is reduced to chloride ions Cl^- in presence of Fe^0 (Xie et al., 2018). Note that the partially oxidized form of iron Fe_3O_4 also exhibits a mild reducing power, resulting from the spontaneous equilibrium between Fe^{2+} and Fe^{3+} in the magnetite structure.

Similarly, chlorinated compounds, such as PCBs, dioxins and most herbicides and insecticides, are suited for chemical reduction. In this case, again, zero-valent metal NPs or bimetallic nanoparticles (combining an electron source with a metal catalyst) are preferentially used (Horváthová et al., 2019). By contrast, polycyclic aromatic hydrocarbons (PAHs) have a deficiency of electron-withdrawing halogen substituents, and consequently exhibit a higher redox potential. Being more electron-rich, they can be degraded following oxidation reactions in which an oxidant is held near the π–electron cloud and receives electrons leading to the formation of a σ–complex precursor to ring opening (Forsey et al., 2010).

Metal oxide NPs, such as CeO_2 and MnO_2, have a pro-oxidant character. They can easily induce oxidative degradation (breaking of carbon-carbon double bonds) stoichiometrically (Védrine and Korotchenkov, 2018). In addition, they release oxygen to form mixed-valent species, such as CeO_x, MnO_x, Fe_3O_4 and $FeMnO_x$, that can participate in catalytic processes. In this case, dioxygen acts as an oxidant and should be activated by adsorption on the bare NPs (that behave like "oxygen sponges") or on hybrid NPs (Au-CeO_2, Pd/Cu-CeO_2, Au-Fe_3O_4) (Corsi et al., 2014; Rani and Shanker, 2018).

Since a single remedial technology is rarely the most effective approach, nanoremediation forms only a segment of the whole cleanup project that may integrate chemical, physical and biological techniques. A synergistic solution would involve the use of several treatment technologies either in combination or sequentially. The latter approach is also termed “treatment train” (Sannino et al., 2017). The bio-cooperative mode of action mentioned above requires an interdependent approach between the nanoparticles and the biota to promote a natural attenuation. For example, highly polluted soils, such as those saturated in mercury, cause changes in soil aeration and moisture, which in turn will result in oxygen depletion. This phenomenon called hypoxia may alter the activity of microbiota and plants that cannot degrade the contaminants independently anymore. When bioremediation is precluded as an option, nanoparticles are needed due to their catalytic behavior and their large surface area to induce/catalyze the physical adsorption of pollutants and initiate their chemical breakdown (Fig. 2).

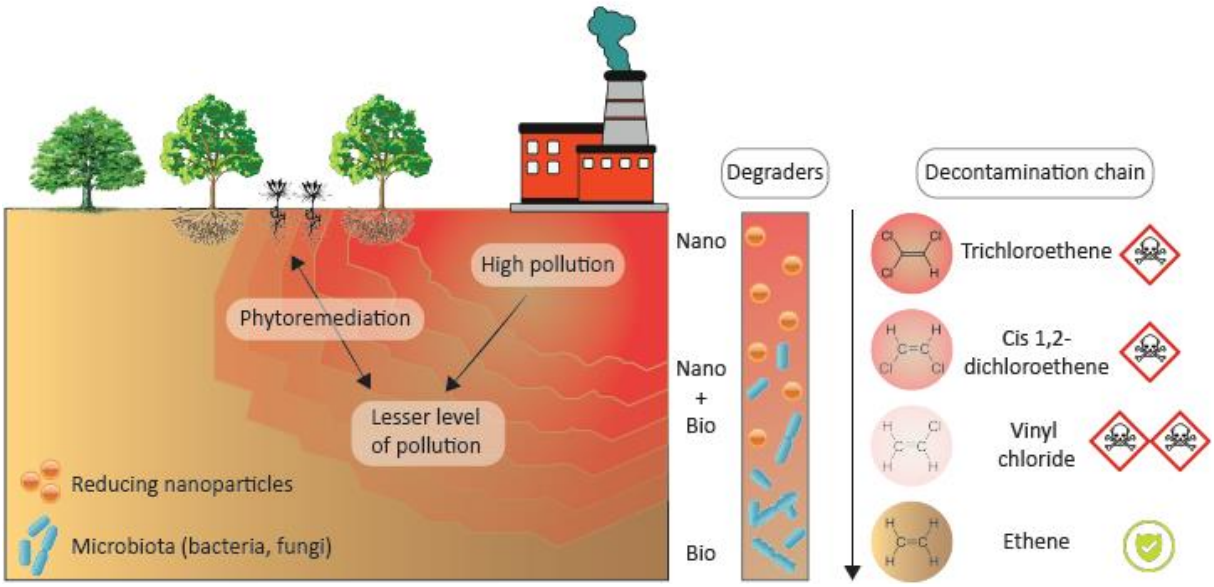

Fig. 2. Synergistic effect between nanoremediation and bioremediation. Example of the chemical reduction of trichlorethene by redox-active nanoparticles to support biological processes.

Lastly, another advantage that must be pointed out is that nanomaterials are prone to transformations in the treated matrix, and can be transformed into innocuous materials (*e.g.* zero-valent iron to goethite).

4.1 Nanoscale zero-valent iron

As a pure academic guide, a search made on the ScienceDirect platform in October 2020 for the word "nanoremediation" yields 208 results. Once restricted to research articles only, this pool narrows down to 125. Among these publications, it turns out that the investigated nanomaterials are predominantly based on nZVI (40 %), followed by iron-based particles such as magnetite, ferrite, Trap-Ox Fe-zeolite, goethite and hematite (35 %), titanium oxide (7 %), silver (7 %), phosphate (6 %) and "marginal" materials such as magnesium aluminate Al_2MgO_4, graphene oxide, cellulose and Cd sulfide (CdS) (5 %). The overwhelming predominance of nZVI among the most studied materials is confirmed by reviewing the ongoing rise of on-site studies. It was estimated in 2009 that nanoremediation was tested in approximately 58 sites around the world, either as pilot or full-scale studies (Bardos et al., 2011). This number successively increased to around 70 sites in 2015, and 100 sites by the end of 2016 (Bardos et al., 2018; Litter et al., 2018). In the most recent listing, no information was available on 9 of these sites. It appears that, of the other 91 sites, a large majority deployed nZVI-based materials (84 sites), the remainder being nanogoethite (3 sites) and nanoscale zero-valent zinc (1 site). No documentation was found concerning the type of material used in the other 3 sites. It is important to point out that 96 % of the treatments were directed at groundwater, even though 22 % also mentioned aquifer or soils, and the last 4 % at soils only.

The synthesis of nZVI *via* the reduction of Fe(II) and Fe(III) salts by sodium borohydride was reported in the 1960s (Oppegard et al., 1961), although the application of nZVI to degrade environmental contaminants was first introduced in 1997 by Wang and Zhang (Wang and Zhang, 1997). To date, the reduction method using borohydride as a reductant is the most studied one because it can be performed in any laboratory. However, when it comes to a large-scale production, the gas-phase reduction of nanoscale iron oxides under H_2 is preferred to prevent pyrophoric reactions of fresh Fe^0 surfaces upon contact with the air (Mackenzie and Georgi, 2019). NZVI has a core-shell structure composed of metallic iron Fe^0 encapsulated in a thin iron (oxyhydr)oxide FeO(OH) shell of a few nanometers thick. The metallic iron core serves as an electron donor (Fe^{2+}/Fe^0 E_0=-0.44V) and exerts a reducing character toward oxidative contaminants, while the oxide shell promotes the adsorption of contaminants *via* electrostatic interactions and/or surface complexation, either facilitating or inhibiting the electron transfer from the core to the outside shell (Ken and Sinha, 2020; Lefevre et al., 2016).

So far, nZVI has been mostly used in the degradation of chlorinated compounds and the reduction of heavy metals. It has also been applied as a catalyst to mitigate a variety of other pollutants of concern, including organochloride pesticides, polychlorinated biphenyls, heavy metal ions and inorganic anions (Mu et al., 2017; Zou et al., 2016). It should be mentioned that the oxide shell is usually generated in controlled atmosphere during the synthesis and acts as a passivation layer, since nano-Fe^0 alone has self-ignition properties in oxygen atmospheres. This high reactivity explains the current research for a wide variety of stabilizing agents, composite particles containing Pd, surfactants and capping agents (*e.g.* carboxymethyl cellulose CMC and aspartate), which may also prevent particle aggregation (Mukherjee et al., 2016).

The high sorption capacity of nZVI is due to the large reactive surface area of the nanoparticles (20-40 m^2/g) while granular (*i.e.* millimeter-sized) Fe used in Permeable Reactive Barriers has a

surface area of less than 1 m^2/g. To a large extent, the reactivity of nZVI is determined by the corrosion of Fe^0 following its exposure to dissolved oxygen and water, resulting in the formation of Fe(II) or Fe(III) species (Ken and Sinha, 2020). Dehalogenation activity depends on the oxidation kinetics of the Fe^0 core and the electron transfer from the core to halogenated organics R-X (Mu et al., 2017):

$$Fe^0 + RX + H_2O \rightarrow Fe^{2+} + RH + X^- + OH^- \quad (1)$$

Additionally, Fe^{2+} is capable of slowly dehalogenating alkyl halides:

$$2Fe^{2+} + RX + H_2O \rightarrow 2Fe^{3+} + RH + X^- + OH^- \quad (2)$$

These equations are expandable to other species such as nitroaromatic compounds ($ArNO_2 \rightarrow ArNH_2$) and heavy metal ions (*e.g.* $Pb^{2+} \rightarrow Pb^0$). Other advantages that can be underlined are: (i) faster cleanup potential compared to conventional techniques due to increased contaminant degradation rates, (ii) higher mobility in aquifers as compared to its microscale counterpart, which enables cleanup of large areas. Table 3 summarizes the main representative results published on the remediation of aqueous solutions and soil samples.

Table 3
Batch experiments demonstrating the removal of contaminants from waters (top column) and soil samples (bottom column) using nZVI.

Media treated	Particle size (nm)*	Pollutants	Reference
Batch tests in aqueous solutions	10-30	Cr(VI) and Pb(II)	(Ponder et al., 2000)
Batch experiments in aqueous solutions	50-65	Uranium UO_2^{2+}	(Crespi et al., 2016)
Aqueous solutions	50-80	Nitrate	(Yang and Lee, 2005)
Aqueous solutions	<5	Trichloroethylene and polychlorinated biphenyls (PCBs)	(Petersen et al., 2012)
Contaminated soil samples	1-50	Polychlorinated biphenyls	(Chen et al., 2014)
Soil samples polluted with tannery wastes	26±17	Cr(VI)	(Singh et al., 2012)
Sandy soils (lab experiment)	15-45	Ibuprofen (anti-inflammatory drug)	(Machado et al., 2013)
Two different soil samples (acidic and calcareous)	60	Pb and Zn	(Mar Gil-Díaz et al., 2014)

* ± Standard deviation if mentioned.

Due to strong attractive interparticle forces, NPs tend to agglomerate and form microparticles, resulting in a limited mobility in porous media. Additionally, the fast formation of oxide layers on the particle surface upon contact with air may limit its efficiency. Consequently, in order to modulate iron reactivity, bimetallic nZVI particles exposing a small fraction (generally 0.1 % w:w) of a noble metal (Pd, Ni, Cu, Pt and Ag) are investigated to enhance their reactivity by increasing the reduction rate, mostly during the dehalogenation of organic pollutants (Bae et al., 2018).

460 Less reactive metal catalysts facilitate electron transfer by associating the enhanced corrosion of Fe and the catalytic hydrogenation properties of the noble metal. In this regard, elemental Pd has been found very effective and the resulting composites achieve faster reaction rates, higher removal efficiency and no accumulation of toxic by-products. Indeed, the primary oxide shell can break down and lead to a loss of Fe^0 content and the formation of a new Fe^{2+}/Fe^{3+} oxide layer (Ulucan-Altuntas
465 and Debik, 2020). Table 4 provides examples of nanoremediation laboratory experiments using bimetallic nZVI. More precisions on bimetallic particles and nZVI supports, such as carbon supports, porous materials like minerals and rectorite, chitosan, polyelectrolyte multilayers, clays and starch, can be found in the following references: (Floris et al., 2017) and (Theron et al., 2008).

470 **Table 4**
Examples of publications illustrating the removal of contaminants from groundwater and soil samples using nZVI variants.

Media treated	Particle	Pollutant	Ref.
Aqueous solutions	nZVI/Pd (0.1-1 %*) NPs 1-50 nm	Chlorinated ethanes	(Lien and Zhang, 2005)
Solution	nZVI/Ni (1→20 %) 10-30 nm	Nitrates	(Kang et al., 2012)
Aqueous solutions	nZVI/Ag (1 %) NPs < 100 nm	Chlorinated benzenes	(Xu and Zhang, 2000)
Contaminated soil samples	nZVI/Pd (0.1 %) NPs 1-50 nm	Polychlorinated biphenyls	(Chen et al., 2014)
Spiked soil	CMC-nZVI/Pd (0.2 %) and aerobic bacteria (*Sphingomonas sp.* Strain)	Lindane (γ-hexachlorocyclohexane)	(Singh et al., 2013)

* By weight.

475 The downsides of most of these studies are typically the use of synthetic water and the lack of insight about the interaction mechanisms between NPs and targeted contaminants. In addition, potential issues (*e.g.* scale up, cost evaluation and downstream recuperation of NPs) are often omitted, even though the investigation of modified and doped nZVI in a laboratory setting is crucial to enhance their *in situ* performance in terms of stability, remediation efficiency and ecotoxicity.

480

4.2 Other types of nanoparticles

Apart from nZVI, NPs typically investigated in water and wastewater treatments are iron-based nanoparticles of different oxidation states (such as magnetite Fe_3O_4), nano-oxides that include TiO_2 and CeO_2, and carbonaceous NPs. Significant and representative results are summarized in Table 5.
485 Other types of NPs, such as fullerene C_{60}, nanostructured minerals, SiO_2 NPs and chalcogenide semiconductors, have been investigated, even if we have decided not to mention them in this review due to the scarcity of available and validated data. However, recent data may be found in the reference (Lofrano et al., 2017).

Table 5
490 Significant results illustrating the removal of contaminants from groundwater and soil samples using NPs other than nZVI and bimetallic NPs.

Media treated	Particle	Pollutant	Ref.
Laboratory	Biogenic magnetite (Fe_3O_4) and maghemite	CCl_4 in anoxic	(McCormick and

experiments	(Fe_2O_3) NPs produced by *Geobacter metallireducens*	conditions	Adriaens, 2004)
Water solutions	γ-Fe_2O_3 NPs 4-18 nm	As(V)	(Tuutijärvi et al., 2009)
Aqueous solutions	Metal modified or Bi^{3+}-doped TiO_2 NPs (16-22 nm)	Nitrates	(Sá et al., 2009)
Aqueous solutions	TiO_2 NPs (4.5 nm) modified with thiolactic acid as a chelating agent	Cd^{2+}	(Skubal et al., 2002)
Aqueous solutions	CeO_2 NPs stabilized with hexamethylenetetramine (12±2 nm)	Cr(VI), Pb	(Recillas et al., 2011)
Batch experiments	CeO_2 NPs (60 nm) / Activated carbon (as adsorbent) composite	Chlorinated hydrocarbons	(Alhooshani, 2015)
Aqueous solutions	CNTs	1,2-dichlorobenzene	(Peng et al., 2003)
Aqueous solutions	Multi-walled CNTs (inner diameter 6-12 nm, outer diameter 20-30 nm)	Pb^{2+}, Cu^{2+}, Cd^{2+}	(Li et al., 2003)

Magnetite (Fe_3O_4) is a magnetic iron oxide that has attracted growing interest in remediation, due to its high adsorptive capacities towards some important water contaminants, notably As^{3+} and As^{5+} (Liu et al., 2015). Additionally, magnetite is receiving attention in soil remediation because it participates in the abiotic reduction of inorganic Hg(II) (Pasakarnis et al., 2013).

Semiconducting oxide NPs such as TiO_2 are used in photocatalytic remediation. Current trends show an increasing interest in solar photocatalysis remediation systems in which TiO_2 NPs are used to convert toxic contaminants into benign products *via* sunlight. Since TiO_2 absorbs only UV light, which is only 5 % of the solar spectrum, particle modifications with organic or inorganic dyes are being investigated to increase the photoresponse window from UV to visible light (Cao et al., 2019). TiO_2 has a wide band gap (3.2 eV for anatase, 3.0 eV for rutile) and generates electron-hole pairs when irradiated with UV light. This charge is then transferable to organic pollutants and induces their oxidation to CO_2 and H_2O as end products (Fig. 3). Additionally, chemisorption of noble metals (Au and Ag) by TiO_2 NPs contributes to increase the process efficiency (Perera et al., 2020). These elements have extremely large absorption and scattering cross-sections in the visible region, and the ability to strongly focus light near their surface. Owing to their localized surface plasmon resonance properties, composite TiO_2-based nanostructures display remarkable features, including enhanced visible light harvesting, hot electron injection and Schottky barriers to trap electrons and prevent recombination (Arshad et al., 2017). Such structures offer new opportunities to overcome the limited efficiency of TiO_2 as solar conversion devices.

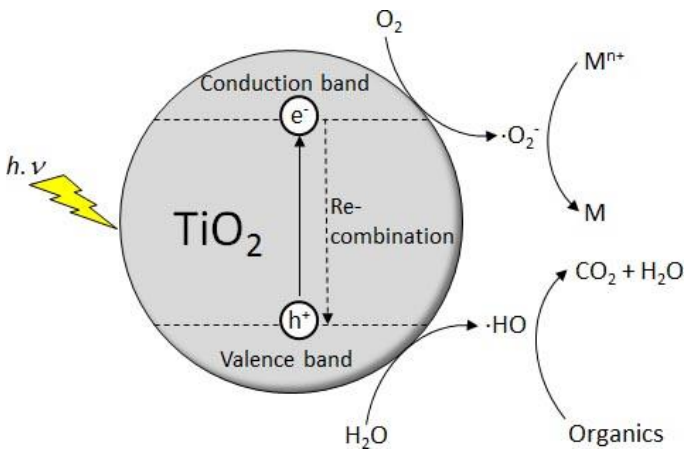

Fig. 3. Structure of a TiO_2 nanoparticle illustrating the photo-oxidation/reduction processes upon UV excitation in the presence of contaminants. Adapted from (O'Carroll et al., 2013).

In the same way, our research group obtained promising results with cerium oxide CeO_2 NPs for the adsorption and removal of Cr(VI) and Pb(II) in synthetic contaminated water. Furthermore, this nanomaterial is redox-active at the nanoscale since Ce^{4+} can easily be reduced to Ce^{3+} on the surface, possesses a high oxygen storage capacity and is capable of decomposing chlorinated organic compounds (Casals, Eudald et al., 2012). The CeO_2 crystal structure contains a large amount of surface defects, mainly due to the reversible removal of oxygen atoms from the surface. Electrons left behind by released oxygen localize on empty f states of cerium ions, switching valence states from Ce^{4+} to Ce^{3+} (Cafun et al., 2013). Consequently, CeO_2 is increasingly being incorporated into composites to improve remediation efficiency.

Among carbonaceous nanomaterials, carbon nanotubes (CNTs), either single- or multi-walled, are promising adsorbent nanostructures, due to their large surface area and tubular architecture. Single-walled CNTs have diameters ranging from 0.3 to 3 nm, while multi-walled CNTs reach diameters of 100 nm. For instance, CNTs have been successfully applied to the sorption of 1,2-dichlorobenzene and heavy metals, with a maximum sorption capacity of 30.8 mg/g (Theron et al., 2008). A possible modification consists of synthesizing CeO_2 supported on CNTs, thus increasing the surface area up to 189 m^2/g. Aside from their ability to sorb heavy metals and organic compounds, CNTs may also be useful as adsorbents for toxins and herbicides in environmental water.

Finally, nanomaterials based on noble metals are currently being investigated to specifically trap organic molecules and promote their complete degradation. An example is the sequential selective adsorption, catalytic reduction and amalgamation of Hg^{2+} from natural wastewater *via* citrate-coated gold NPs (Ojea-Jiménez et al., 2012).

5. Fate of nanoparticles in the environment

The high surface-to-volume ratio and reactivity of NPs make them extremely dynamic in environmental systems governed by a global hydrologic cycle interconnecting soils, ground and surface. As a reminder, groundwater is found in two zones: (i) the unsaturated zone, immediately below the land surface, which contains water and air in the open spaces (or pores), (ii) the underlying saturated zone, in which every pore and rock fracture is filled with water (Cushman and Tartakovsky, 2017). Consequently, the movement of contaminants or nanomaterials between both environmental media can be described as a preferential flow through the pore spaces from one sub-matrix (defined by pore density and permeability, inorganic and organic contents, etc.) to another.

The behavior of nanomaterials within a matrix is comparable to that happening in living organisms: a nanoparticle injected in a patient's bloodstream will be covered by a dynamic protein

bio-corona in a matter of seconds, and its fate will be subsequently governed by reactions occurring at the triple interface nanoparticle/bio-corona/blood (Casals et al., 2010). Similarly, nanomaterial transport in porous media can be described by three mechanisms: (i) direct interaction of NPs with soil components, (ii) sedimentation due to gravity and (iii) diffusion due to Brownian motion (Lecoanet et al., 2004). Along the way, the particles may be subjected to three types of transformations: 1) chemical (reduction/oxidation, photooxidation and photoreduction, dissolution and sulfidation) through interactions with natural and/or anthropogenic chemicals, 2) physical (aggregation) and 3) biotic transformations (*e.g.* redox reactions in bacteria) (Fig. 4).

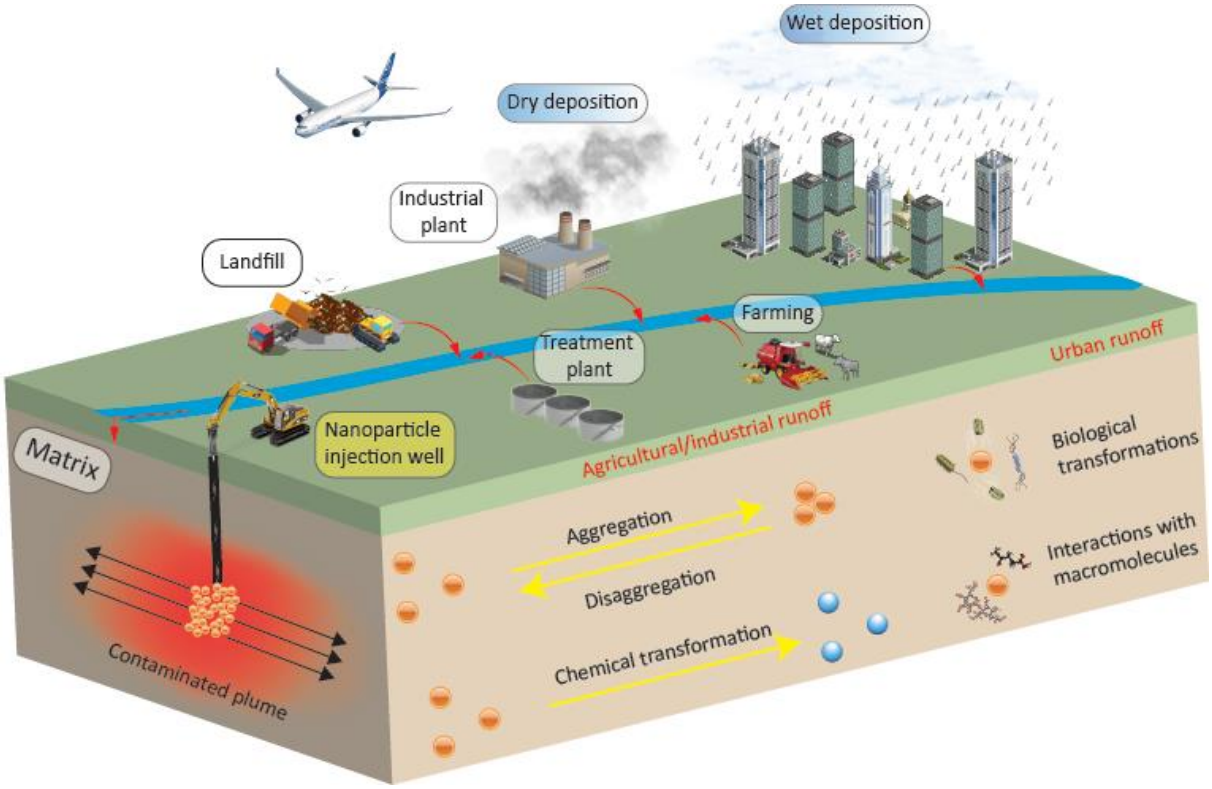

Fig. 4. Schematic representation of the contamination in the environment, depicting the key processes determining the fate and behavior of nanoparticles in environmental matrices following injection. Adapted from (Lefevre et al., 2016).

The most prominent modifications are aggregation and dissolution. Generally, aggregation is likely to occur early after the injection step, while the NP concentration is locally high; the release point may thus contain concentrations high enough to result in homoaggregation and then, following interactions with other constituents, in heteroaggregation.

Beyond aggregation, NPs are also prone to chemical transformation, like increase of valence state (oxidation, sulfidation and corrosion). Indeed, another critical factor that can affect the efficiency of nanoremediation strategies is the propensity of particles to dissolve. The dissolution profile strongly depends on the size of the particles, their physicochemical surface properties and their environment, especially for NPs smaller than 20-30 nm wherein interfacial effects (known as Gibbs-Thomson effects) dominate. Due to the high surface energy of NPs, the dissolution phenomenon is often amplified. Garner and Keller reported the dissolution time frames of NPs in different water types. It turned out that coated nZVI, ZnO and Ag were generally dissolved within weeks while other types of particles such as Au, CeO_2, CuO and TiO_2, remain in particulate form over periods of several months (Garner and Keller, 2014).

After injection, surface oxidation of iron-based NPs such as nZVI always happens, resulting in the formation of a particle composed of a Fe^0 core surrounded by an iron(hydr)oxide layer, which will

quickly thicken over time (Crane and Scott, 2012). The initial release of Fe^{2+} (and Fe^{3+} in a lesser way) will be followed by a progressive oxidation to insoluble iron species such as maghemite (Fe_2O_3), magnetite (Fe_3O_4) and lepidocrocite (FeOOH), amongst others. If the use of stabilizers (*e.g.* polyacrylic acid, polyaspartate, chitosan or sodium oleate) has undoubtedly improved the colloidal stability of NPs, biotic and abiotic degradation will ultimately remove particle coating. Regarding other nanomaterials, it has been reported that silver NPs can be oxidized and sulfidized in the environment, resulting in a modification of their aggregation state, surface chemistry, and charge as well as their ability to release toxic Ag^+ ions (Levard et al., 2013). By contrast, gold NPs interact with humic substances, resulting in a passivating nanoscale layer (Diegoli et al., 2008), very similar to bio-coronas in mammalian systems, that dramatically changes their aggregation, deposition and toxicity properties (Lin et al., 2017).

The extent of these transformations will thereafter alter the fate, transport, toxicity and remediation efficiency of nanomaterials. These parameters are paramount since, to develop safe remediators, the best risk-to-benefit ratio is obtained by balancing dynamic and kinetic aspects. This recalls a pharmacological-like approach in which pharmacodynamics (the impact of the NP on the pollutant) must be correlated to pharmacokinetic aspects (the impact of the pollutant on the NP, inducing changes in morphology and surface charge together with valence state switches, amongst others).

However, the complexity of environmental conditions and the specificity of contaminated sites prevent the development of a unifying model of NPs´ fate in the environment. Fortunately, some studies mentioned afterwards help setting marks to apprehend their behavior.

5.1 Deposition in soils

To date, only limited research has focused on the interactions between NPs and soil components, including their subsequent fate as part of a remediation approach. One of the main reasons is the complexity of soil systems, composed of a heterogeneous mixture of gas, liquid and soil phases (including organic matter and microbial communities), explaining why most of the recent studies are conducted on a case-by-case basis and do not allow yet to draw extendable conclusions (Liu et al., 2015). The major difficulties are experienced in unsaturated soils (*i.e.* when the pores between soil particles are partially filled with water).

More specifically, the fate of NPs is guided by the interdependence of their intrinsic physicochemical characteristics, and the combined presence of humic substances – the primary organic components of soils – and natural suspended colloids (organic particles, clays and phyllosilicates) forming a coating around the suspended minerals. Indeed, slurry pH and ionic strength have an impact on both the precipitation of dissolved humic substances and the dissociation of functional groups of humic acids that could subsequently modify the charge of some NPs. The extent of these modifications will determine the inter-particle repulsive forces and, in turn, define the NP deposition pattern (fast *versus* slow) (Dror et al., 2015). Transport will happen, provided that the forces causing NP attachment to soil particles are minimized. Otherwise, homo/hetero-aggregation and deposition will primarily govern NP transfer from the land surface to groundwaters. After injection, NPs can interact with soil constituents or be directly sequestered within the soil pores. This point is paramount: NPs which are strongly sorbed to soil constituents will therefore be immobilized and clog soil pores. On the other hand, NPs small enough to fit into small spaces between soil particles will travel farther than larger particles, before being trapped in the soil matrix (Fazeli Sangani et al., 2019).

It should be mentioned that these modifications go both ways because humic substances are also transformed following contact with NPs. For instance, it was observed that the native structure of humic acid extracted from peat soil is modified by TiO_2 NPs (Yang et al., 2009). In the same way, NPs impact soil hydraulic properties. The mechanisms of adsorption involved are presumably anion

exchange following electrostatic interactions, ligand exchange, hydrophobic interactions, hydrogen bonding and cation bridging. Taken together, this set of interactions deeply influences the retention capacity of contaminants in NP-amended soils through particular sorption profiles.

A concern is getting the nZVI to the contamination zone, before it forms clusters too large to move underground, and to ensure that the particles do not react with water and/or oxygen before reaching the contaminant. If that happens, the particles may not actually reduce a chemical to an innocuous substance. In this regard, more details regarding the fate of nZVI as a function of particle concentration, size distribution and zeta potential can be found in the reference (Keane, Emily, 2009). This dynamic state constitutes a serious issue: if the nZVI particles are specifically designed to improve their dispersability while limiting their aggregation and slowing down passivation to ensure maximum efficiency, the mechanism of remediation itself underlies the loss of their nano-character (*i.e.* transformation from Fe^0 to Fe^{2+}). Hence, soil hydraulic properties and injection technologies are of the utmost importance. It is desirable that the injected nZVI remain immobile once delivered, thus leading to the gradual transformation into iron minerals that will theoretically remain stationary in the soil matrix (Zhao et al., 2016).

5.2 Injection in groundwater

From an *in situ* remediation standpoint, the transport of NPs must fulfill the following conditions: (a) NPs should circulate into the subsurface, *i.e.* they should be mobile under a defined injection pressure to ensure delivery into the contaminated zone, and (b) NPs should then be virtually immobile or confined under natural groundwater flow conditions, *i.e.* once the external injection pressure is released (Liu et al., 2015).

In this regard, aggregation phenomena are paramount. Garner and Keller summarized the aggregation time frames of NPs in different types of water, including storm-, fresh-, sea and groundwater (Garner and Keller, 2014). Interestingly, groundwater shows the most variable results with fast-aggregating NPs (within hours) such as FeO/Fe_2O_3, coated nZVI and ZnO, while others remain relatively stable over days (CeO_2, CuO and TiO_2) and weeks/months (Au, C_{60}, FeOOH, SiO_2 and SWCNTs). In addition to intrinsic NP properties, these variations are probably caused by the high variability of ionic strength, the presence of organic matter in groundwater and distinct affinities between humic substances and NPs. Note that many experiments were conducted using artificial groundwater under biased aggregation conditions (Cai et al., 2020).

More specifically, materials derived from nZVI have shown a significant tendency to aggregate, indicating that particles are either confined in groundwater contamination plumes, thus preventing offsite transport, or quickly precipitate out of the groundwater upon oxidation. For instance, 30−70 nm nZVI rapidly aggregates in water to form micrometer-sized clusters, greatly reducing their mobility in the subsurface (Duan et al., 2018; O'Carroll et al., 2013). Similarly, TiO_2 NPs, when placed in aqueous solutions under conditions of pH and ionic strength that replicate those of soils, interact rapidly (in a matter of minutes) to produce micro-aggregates (French et al., 2009).

Other studies on nZVI mobility have demonstrated how the rate and degree of oxidation are also key factors largely influenced by the environmental conditions. Reinsch et al. showed that nZVI injected in simulated groundwater tend to be quickly oxidized by dissolved oxygen, leading to the formation of maghemite and magnetite within the oxide layer (Reinsch et al., 2010). Among the anions commonly found in groundwaters (bicarbonate, chloride, sulfate, etc.), only nitrates prevented the oxidation of nZVI by passivating the surface. In the same way, Johnson et al. investigated the field-scale mobility, transformation and fate of CMC-stabilized nZVI during subsurface injection in a model aquifer, including several layers of sand and clay (Johnson et al., 2013). While stabilized nZVI were transported over up to 2.5 meters under aggressive flow

conditions, unoxidized nZVI were carried only about one meter, confirming the importance of the interaction between particles and oxidizing agents present in groundwater.

The interaction with groundwater components, namely natural organic matter (NOM) and a complex assortment of ions (*e.g.* Ca^{2+}, Mg^{2+}, K^{+}, Na^{+}, Cl^{-}, HCO_3^{-} and SO_4^{2-}), has also an important impact on NP behavior (Pelley and Tufenkji, 2008). Natural organic matter is a complex matrix of slightly water-soluble organic materials. It is a key component in aquatic environments that derives from decaying plants and animal matter. This includes mostly humic fractions, composed of high molecular weight organic molecules such as humic acids (HA) and fulvic acids. These constituents, in addition to tannic acid, represent the major fraction of dissolved organic matter (DOM) in water. They are oxidized very slowly and their solubility in water may vary with pH (Olk et al., 2019). It was reported that the stability of metal oxide NPs such as TiO_2, CeO_2 and ZnO was reduced in groundwater samples due to the adsorption of NOM on their surface (Keller et al., 2010).

It must be understood that ions in solution have a tendency to screen the surface charge of NPs, potentially promoting their aggregation. In the meantime, the high surface energy of NPs leads to the adsorption of organic matter, forming a protective and stabilizing coating, as observed in biological media (Bastús et al., 2008). If the coating is fully formed, it contributes to enhance colloidal stability, thanks to steric effects. However, if the coating is partial, the organic matter adsorbed on a NP may also be adsorbed onto the free surface of another partially coated particle, resulting in a crosslinking phenomenon which leads to the formation of composite aggregates (Barbero et al., 2017). The screening effect of ions depends on their Debye length, also described as the Hofmeister series when considering how they affect the solubility of proteins (Neagu et al., 2001). Similarly, the fate and solubility of NPs will be determined by the solubility of the organic coating, as much as its adsorption kinetics.

This explains the aforementioned lack of stability of metal oxide NPs in groundwater systems exhibiting low NOM concentrations (0.1-2 mg/L), while the high NOM concentrations typically found in surface waters (>1 mg/L total organic carbon) are sufficient to provide steric stabilization once adsorbed onto the particles. Thus, the impact of HA in groundwater varies in function of the type of particle surface modification. The adsorption of HA onto nZVI enhances the stability of nZVI coated with polyacrylic acid, although it induces aggregation when the same particles are modified with Tween-20 or starch (Dong and Lo, 2013). However, the eventual tendency of nZVI to aggregate cannot be explained by the presence or absence of HA only. In this regard, studies performed under realistic environmental conditions suggest that nZVI have a strong tendency to aggregate in ultrapure water, forest spring water and landfill leachate (Peeters et al., 2016).

Nowadays, there is much debate on whether or not NPs can be effectively transported by groundwater to impact an entire contamination plume, and if highly-mobile particles will move offsite and become a toxicological issue. Therefore, understanding the transformation of NPs upon release into the environment is critical to evaluate their potential efficiency, as well as their adverse effects (Lefevre et al., 2016; Lowry and Casman, 2009; Mukherjee et al., 2016). A solution could be to pre-incubate the NPs with organic matter taken from the relevant environmental matrix.

5.3 Field applications of nZVI

The first field injection test of bimetallic nZVI/Pd NPs was reported in 2001 for the degradation of trichloroethylene (TCE) and other chlorinated aliphatic hydrocarbons in groundwater (Elliott and Zhang, 2001). Particles between 100 and 200 nm in size were injected at a manufacturing site over a two-day period. The authors observed a TCE reduction of up to 96 % within 4 weeks. In 2005, Quinn et al. demonstrated the nZVI-assisted dehalogenation of dense nonaqueous phase liquids (DNAPLs) on a NASA launch site (Cape Canaveral, Florida) (Quinn et al., 2005). Injection of surfactant-stabilized

particles (100-200 nm) into the saturated zone was followed by the degradation of trichloroethene contained in soil and groundwater within the test area, resulting in the production of *cis*-1,2-dichloroethene, vinyl chloride and ethene. A significant reduction in TCE soil content (>80 %) was observed within 90 days, concomitantly with a significant reduction in groundwater concentration (57-100 %) over 5 months. Ten years later, Bardos et al. reported 70 projects documented worldwide at pilot or full scale (Bardos, P, 2015). Most of the studies focused on the degradation of chlorinated solvents for plume management, while pilot studies demonstrated successful treatments of BTEX (benzene, toluene, ethylbenzene and xylene), perchlorates, Cr(VI), diesel fuel, PCBs and pesticides. The majority of applications have used direct injections of nZVI supplied as liquid slurries.

The primary mechanism of action is assumed to be an abiotic degradation (*i.e.* through hydrolysis and photolysis) linked to the particle assemblies. Henn and Waddill complemented these observations in a pilot study using Pd-catalyzed and polymer-coated nZVI (50-600 nm) based on a proprietary formulation to decontaminate a source area containing VOCs (Henn and Waddill, 2006). A 65 to 99 % reduction in concentration of parent compounds (trichloroethene and 1,1,1-trichloroethane) was observed, due to abiotic degradation within five weeks; it was further accompanied by the formation of less hazardous daughter products (ethane and acetylene). However, it appeared that the concentration of these intermediates increased in some wells, while it persisted in others. Several reasons, such as an insufficient amount of injected nZVI, a heterogeneous geology profile or a premature iron passivation, were given. Additionally, long-term observations (6-9 months) showed that biological degradation eventually followed the particle-assisted degradation.

The importance of bioremediation triggered by the presence of nZVI was further investigated by Sheu et al. in a pilot-scale study involving tetrachloroethene (PCE)-contaminated groundwater (Sheu et al., 2016). NZVI caused the degradation of PCE to daughter components and led to the growth of *Dehalococcoides* spp. and *Desulfitobacterium* spp. under anaerobic conditions, further accelerating the PCE dechlorinating rate. Indeed, iron homeostasis is critical for microorganisms since Fe^{2+} and Fe^{3+} are essential in a wide variety of important metabolic processes. For example, iron oxide NPs were used as an iron mineral tank to promote the growth of anaerobic microbial consortia (Casals et al., 2014). In this particular case, the nanomaterial provides iron ions to the bacterial siderophores – high-affinity iron-chelating compounds that serve to transport iron across cell membranes – in an analogy with the drug called Ferumoxytol used for the treatment of iron deficiency anemia in adult patients based on the same principle (Schwenk, 2010).

Similarly, Su et al. carried out a field-test evaluation to remediate chlorinated volatile organic compounds (CVOCs), mostly tetrachloroethene and chlorinated daughter products, contained in subsurface-source zones using corn oil and emulsified particles (35-140 nm, specific surface area 30 m^2/g) (Su et al., 2012). An 86 % reduction in the weight of CVOCs was observed over 2.5 years. Studies were not confined to chlorinated compounds though. For instance, a pilot test combined the chemical reduction of Cr(VI) in groundwater using nZVI and the subsequent biotic reduction supported by whey (Němeček et al., 2015). Interestingly, the authors detailed the transformations affecting the NPs: (i) nZVI were first oxidized to Fe(III), while reducing Cr(VI) to the less toxic Cr(III) during the abiotic phase, and (ii) were then subjected to a microbial reduction back to Fe(II) to act as a reducing agent for Cr(VI) again, hence a partial recycling.

In a thorough and complex work, Macé et al. analyzed and cross-compared the pilot field tests performed between 2003 and 2005 in Europe and North America; nZVI was effective in reducing Cr(VI) and chlorinated solvents from groundwaters (Macé et al., 2006). It turned out that the concentrations of chlorinated solvents decreased greatly within a few days. When present, sulfates and nitrates also decreased, although the effect of nZVI was subsequently diminished. The authors stressed the primary importance of (i) determining prior to injection the site-specific geological, hydrogeological, and geochemical conditions (*e.g.* fractured rock or porous media), (ii) monitoring

geochemical parameters during the tests, and (iii) carefully selecting particles´ reactivity (since more reactive nZVI are consumed faster).

Furthermore, nZVI were used to remediate contaminated soils. In a pilot-scale test, 625 nm CMC-stabilized nZVI were injected in soils contaminated with CVOCs (mostly PCE, TCE and chloroform) (Kocur et al., 2015). The test site was formed of a heterogeneous subsurface composed of clayey sand and sandy areas adjacent to a former CVOC production facility. As in groundwater treatments, the composition of CVOCs shifted toward less chlorinated compounds over 3 weeks. More precisely, in the 10 days following nZVI injection, the total CVOC content decreased by 20 % in some wells, and the parent compounds decreased to less than 10 % of the total CVOCs. A period of abiotic degradation was followed by a period of enhanced biotic degradation, suggesting that the injection of particles induced the stimulation of organo-halide respiring microorganisms.

Still, recent studies have shown the limited soil mobility and deliverability of bare nZVI, resulting in the search for more stable particles (Crane and Scott, 2012). Due to strong attractive interparticle forces, nZVI tend to increase in size, yielding agglomeration up to the formation of micron-sized particles, thus resulting in a limited mobility in porous media (O'Carroll et al., 2013).

The number of actual applications of nZVI is increasing rapidly, although only a fraction of the pilot and field tests have been reported. Indeed, data obtained from companies are not necessarily collected as part of research projects, resulting in incomplete data. An overview of pilot surveys and full-scale tests can be found in references (Mueller et al., 2012) and (Bardos et al., 2015).

6. Ecotoxicity of nanoremediators

The development of new tools in the environment is not free from risks. While NPs can degrade pollutants, the exact same mechanisms involved may prove toxic to biota. Such side effect is susceptible to occur both for the pristine NPs and their derivatives during speciation. This aspect is part of a bigger picture, since the successful introduction of this new technology is subject to technical and societal imperatives: interacting physically and chemically with environmental matrices without impacting the local biota, while making it acceptable to society.

The surface of NPs experiences constant modifications as they evolve through the environment, hence a particle response that can be extremely complex and diverse. Questions have frequently been raised once NPs intended for remediation are injected in soils and groundwaters: how mobile are the particles? Do the particles have the capacity to carry pollution towards new and unintended environmental compartments? Is their transformation susceptible to destroy or rather stimulate biota (Lowry and Casman, 2009)? And, consequently, what is their adverse impact on the environment in terms of bioaccumulation, persistency and long-term changes in microbial communities? For example, if the particles are unable to entirely reduce a chemical such as trichloroethylene in carbon dioxide and water, what might be left behind is a much more toxic chemical such as vinyl chloride, a carcinogenic compound that is toxic even at low doses.

6.1 Impact of nZVI and iron-based particles

Nanoscale zero-valent iron (nZVI) is a compelling illustration of the ecosafety challenges associated with nanoremediation. For instance, Rede et al. showed that using nZVI to treat an ibuprofen-contaminated soil had a negative impact in the germination and development of lettuce seeds (Rede et al., 2016). These results indicate that soil nanoremediation treatments might be, under certain circumstances, more prejudicial for terrestrial organisms than contaminated soils. By contrast, Fajardo et al. observed no negative effects on the properties of soils (pH, conductivity,

organic matter, etc.) polluted by heavy metals (Pb and Zn) after exposure to aged nZVI (Fajardo et al., 2015).

Moreover, the injection of nanomaterials, regardless of the medium, always impacts the physicochemical properties of the matrix along the pathway. For example, Elliott et al. observed that bimetallic nZVI/Pd NPs caused groundwater pH to increase temporarily from 5.1 to 7.7 during field injection tests (Elliott and Zhang, 2001). This effect is due to the reaction of zero-valent iron with water while being oxidized to Fe^{2+}. The authors also reported a reduction of the redox potential from +150 mV to +100/-350 mV (depending on the piezometer locations) before recovery, indicating more reducing conditions. Furthermore, nZVI particles are known to decrease dissolved oxygen over several days as a result of their rapid oxidation, leading to the formation of both maghemite and magnetite.

The oxidation of nZVI is a naturally occurring phenomenon caused by the interaction with an oxidizing agent that can be oxygen, water or the targeted pollutant itself. During this process, Fe(0) is gradually oxidized to soluble Fe^{2+} and Fe^{3+} ions, leading to the formation of a structure composed of a Fe(0) core and an iron oxide layer. Kumar et al. showed that, if lepidocrocites and goethites are primarily formed under oxic conditions, the depletion of oxygen furthers the oxidation up to the formation of maghemite nanoparticles (Kumar et al., 2014). The oxidation chain can be summarized as follows: $Fe(0) \rightarrow Fe(OH)_2 \rightarrow Fe_3O_4 \rightarrow (\gamma\text{-}Fe_2O_3)$. As said earlier, Fe^{2+} and Fe^{3+} ions are continuously released upon injection of nZVI in the environment. What can be the impact of such variations on microorganisms?

6.1.1 Potential adverse effects on microbiota

Microorganisms are the foundation of all known ecosystems, serving as the basis of food webs and the primary agents of global biogeochemical cycles. It is estimated that almost 90 % of soil biological activity is carried out by bacteria and fungi (Nannipieri et al., 2003). Bacteria abound in soils and are critical to (i) decompose organic residues and to recycle soil nutrients and (ii) produce polysaccharides that cement sand, silt and clay particles together to improve soil structure, water infiltration and water retention capacity. Since soils, surface waters and groundwaters are interrelated, bacteria (mostly Gram-negative) are also present in groundwaters, characterized by the absence of light as well as low organic carbon and nutrient availability. This means that bacteria found in groundwaters preferentially use inorganic electron donors and light-independent chemical reactions as a source of energy. For example, lithotrophic bacteria convert nitrogen, sulfur and iron into energy and are an essential part of the nitrogen cycle and pollutant degradation. Consequently, studies aimed at determining the impact of NPs on bacterial populations and the underlying processes are paramount, since an ill-controlled nanoremediation might disrupt soil or water integrity.

As a matter of fact, resident bacteria are the first living organisms to be exposed to nZVI and are directly affected during the remediation process. Most studies used *in vitro* toxicity assays to measure cell viability and integrity, cell growth and/or biological activity of the exposed microbial species (Table 6). However, the data obtained suffer from the intrinsic limitations of *in vitro* methodologies. The doses used are often extremely high and sometimes even higher than doses used for pilot-scale remediation applications (*e.g.* 2 g/L for the removal of Cr from groundwater (Němeček et al., 2014)). As mentioned by Semerád et al., a nZVI concentration in the range of unit grams per liter can only be found in the injection boreholes, while the surrounding environment is exposed to concentrations that are at least an order of magnitude lower due to the limited mobility and gradual consumption of nZVI (Semerád and Cajthaml, 2016).

Generally, nZVI has been reported to be strongly toxic toward bacteria such as *Pseudomonas fluorescens*, *Pseudomonas putida*, *Alcaligenes eutrophus*, *Agrobacterium* sp. *PH-08*, *Escherichia coli*, *Bacillus nealsonii*, *Bacillus subtilis*, *Bacillus cereus* and *Paracoccus* sp. *YF1*, amongst others (for a review, see (Lefevre et al., 2016), (Semerád and Cajthaml, 2016) and (Kotchaplai et al., 2019)). The first study on nZVI toxicity to bacteria was published in 2008 by (Lee et al., 2008). The authors showed that nZVI up to a concentration of 120 mg/L inactivated *E. coli* within 1 hour under deaerated conditions. Inactivation was less important under air saturation due to the corrosion and surface oxidation of zero-valent iron by dissolved oxygen. Physical disruption of the cell membranes was observed and, more importantly, Fe(II) was suspected to react with microbial intracellular oxygen or hydrogen peroxide to produce reactive oxygen species. This hypothesis was substantiated in later studies : it turns out that nZVI oxidation is enhanced in presence of hydrogen peroxide (H_2O_2) contained in microbial cells to generate highly reactive oxygen species, such as hydroxyl hydrogen radical ($OH^{\bullet}$), superoxide ($O_2^{\bullet-}$) or ferryl ion (FeO^{2+}), *via* Fenton chemistry (Ševců et al., 2011). These species are known to play a significant role in nZVI toxicity, causing serious damages to cell membrane integrity and respiratory activity (Kim et al., 2010).

In terms of cellular activity, it was demonstrated that nZVI induced in *Pseudomonas stutzeri* a significant increase in the expression of KatB, an enzyme involved in cellular oxidative stress detoxification (Saccà et al., 2014). In addition, damages to cell wall components affected cellular response by provoking a downregulation of membrane proteins and an upregulation of the proteins involved in the reduction of intracellular oxidative stress. Interestingly, the behavioral response of *P. putida* G7 to nZVI was evaluated by Ortega-Calvo et al. as a new approach to evaluate the stress induced by nanomaterials (Ortega-Calvo et al., 2016). The authors observed that the bacteria exhibited a specific mode of swimming characterized by random changes of direction in the absence of nZVI, while exposure to nZVI induced a distinct swimming behavior, characterized by much more frequent and abrupt changes of direction. A complementary study showed that nZVI tended, upon short-term exposure, to accumulate and penetrate the bacterial cell membrane, the composition of which switched from the *cis* to the *trans* isomer of unsaturated fatty acid, resulting in a more rigid membrane counteracting the membrane-fluidizing effect of nZVI (Kotchaplai et al., 2017).

Among other factors, it was also found that the toxicity of nZVI depended on the bacterial growth phase (Chaithawiwat et al., 2016a). A higher resistance to nZVI was observed in *E. coli* and *P. putida* during the lag phase (*i.e.* when the cells are metabolically active and increase only in cell size) and the stationary phase after the maximum population was reached. By contrast, cells during the exponential (growth) phase and the decline (death) phase exhibited a lower resistance to nZVI. The reason may be that the levels of the transcription factor rpoS, a central regulator of the general stress response, are about four-fold higher in stationary phase than in exponential phase (Yuste et al., 2006).

Furthermore, the oxidation state of iron atoms in nZVI and iron-based NPs have been shown to influence cytotoxicity toward *E. coli* (Auffan et al., 2008). Nano zero-valent iron, as a mixture of Fe(0), Fe(II) and Fe(III), was the most toxic material, while magnetite Fe_3O_4 (mixed Fe(II)/Fe(III)) exhibited a lesser toxicity and maghemite (all Fe(III)) no toxicity at all. It should be mentioned, though, that maghemite, despite its physicochemical stability, was toxic toward a mutant strain of *E. coli* devoid of superoxide dismutase activity (enzymes that catalyzes the partitioning of superoxide radicals), indicating a slight oxidative stress effect but only for very large amount of NPs.

The extent of the oxidation of the Fe(0) core is paramount regarding particle toxicity. It has been demonstrated that nZVI, upon injection into the environment, is oxidized under both oxic and anoxic conditions (Mylon et al., 2010; Tanboonchuy et al., 2011). However, the toxicity of nZVI under oxic conditions is significantly lower than under anoxic conditions, because of the formation of a passivating iron oxide layer resulting from mild surface oxidation. Indeed, the lifetime of nZVI (*i.e.*

until nZVI reaches complete oxidation) under aerobic conditions can be as short as 2 hours, while nZVI can take several months to be entirely oxidized under anaerobic conditions. This point is supported by a study where the complete oxidation of nZVI under aerobic conditions eliminated its bactericidal effects (Li et al., 2010). This indicates that the percentage of zero-valent iron is directly related to nZVI cytotoxicity.

In the same study, the effect of surface coatings was investigated since the presence of surfactants, polymers or any functional group attached to the surface of nanoparticles may induce physicochemical changes that will affect their cytotoxicity. It appears that nZVI coated with polystyrene sulfonate, polyaspartate and natural organic matter (NOM) significantly mitigated the detrimental effect toward *E. coli* through a reduced interaction between particles and microorganisms. Additionally, carboxymethyl cellulose (CMC)-stabilized nZVI were shown to exert a minimal oxidative stress response and to slow disruption of cell membrane integrity, resulting in a reduced cytotoxicity against *Agrobacterium sp.* PH-08, as compared to uncoated nZVI (Zhou et al., 2014). Furthermore, Chen et al. investigated the role of NOM in the microbial toxicity of nZVI, concluding that the surface modification of nZVI might alter the physicochemical interactions with organisms and influence both toxicity and bioavailability, probably due to electrosteric hindrance effects (Chen et al., 2011). In the same way, Zhang et al showed that nZVI modified by sodium alginate (a natural polysaccharide) and bentonite (a type of ubiquitous clay) exhibited a lower toxicity toward *E. coli* (M. Zhang et al., 2020).

Recently, a sulfide coating has attracted a lot of attention as an alternative to overcome the limitations of nZVI (*i.e.* agglomeration and passivation) while preserving its reactivity. In this regard, Cheng et al. (2019) investigated if sulfidation would have a negative effect on the growth of *E. coli* (Cheng et al., 2019). Particles with the highest sulfur content (Fe/S molar ratio of 10), once incubated with the bacteria at a concentration of 10 mg/L for 1 hour, were less toxic than nZVI (2.14 *versus* 2.95-log reduction in viable cells), even though this level of toxicity is not negligible. However, the authors showed that both nZVI and sulfide-nZVI aged for 30 days exhibited a negligible toxicity (<0.15-log).

Following this study, Semerád et al. showed that the toxicity on the Gram-negative bacterial strain *P. putida* CCM 7156 decreased with increasing sulfur content (mass ratios S/nZVI from 0.25 to 5 %) (Semerád et al., 2020). This tendency probably originates from the shielding effect of the sulfur present in the shell that prevents the release of iron ions to the surrounding media. However, an aging experiment over 60 days showed that 100 mg/L sulfide-nZVI caused a substantial oxidative stress between 7 and 14 days, reaching a level similar to the one caused by bare nZVI. This phenomenon remains unexplained since the toxicity was not caused by dissolved sulfur (H_2S, HS^- and S^{2-}), as checked by the authors using ICP-MS.

By contrast, exposure to nZVI concentration as high as 10 g/L had no effect on Gram− *Klebsiella oxytoca* (Saccà et al., 2013) and *Klebsiella planticola* DSZ (Fajardo et al., 2012), both found in water and soil. In the latter study, though, the authors comparatively observed a severe toxic effect on Gram+ *B. nealsonii (*0.8-log reduction after 24 h). This difference in reactivity between Gram− and Gram+ bacteria was underlined by further studies showing that Gram+ *B. subtilis* was more tolerant to nZVI than *E. coli* (Chen et al., 2011; Yoon et al., 2018) or *P. fluorescens* (Diao and Yao, 2009). Three reasons can be given to explain this : i) Gram+ bacteria are surrounded by layers of peptidoglycan many times thicker (20-80 nm (Madigan et al., 2017)) than in Gram− bacteria, ii) the higher negative charge of *B. subtilis* compared to *E. coli* (32.5 *versus* 26.9 mV) probably contributed to a higher electrostatic repulsion and reduced toxicity with negatively charged nZVI diluted in usual buffers such as $NaHCO_3$ (Raychoudhury et al., 2010), and iii) only Gram+ bacteria, including *B. subtilis*, possess an

enzyme called nitric oxide synthase whose ability to produce nitric oxide subsequently reactivates catalase, a major antioxidant enzyme (Gusarov and Nudler, 2005).

It should be noted that, if nZVI has been often used in the form of bimetallic nanoparticles, information on the toxicity of such composites has been scarce. Murugesan et al. designed a nano-bio hybrid process for the remediation of 2,4,4'-trichloro-2'-hydroxydiphenyl ether, a contaminant known as triclosan, by combining nZVI–palladium bimetallic nanoparticles (nFe–Pd) and *Sphingomonas sp.* PH-07, a bacterial strain that can utilize diphenyl ether as sole source of carbon and energy (Murugesan et al., 2011). Cell turbidity measurements showed that the bacteria grew well for concentration of nanoparticles up to 0.1 g/L, whereas bacterial growth was drastically inhibited for concentrations between 0.1 and 0.5 g/L. It must be emphasized that the authors observed at 0.1 g/L a delayed growth (~30 %) during the exponential phase, before a return to normal growth. Unfortunately, this study does not present comparative information between the toxicity of nFe-Pd and nZVI. In this regard, Kim et al. assessed the potential toxicity of various bimetallic Fe nanoparticles (Fe/Pd, Fe/Cu, Fe/Ni, and Fe/Pt), synthesized by displacement plating of nZVI with metal salts in solution, toward *E. coli* and compared them with unmodified nZVI (Kim et al., 2014). The results showed that Fe/Cu was the most toxic at concentrations ranging from 10 to 500 mg/L, followed by Fe, Fe/Ni, Fe/Pt, and Fe/Pd nanoparticles in descending order. Additionally, toxicity was correlated with an increase in the production of reactive oxygen species.

Besides, it was of high importance to understand the relationship between the redox state of iron-based nanoparticles and their cytotoxicity toward model organisms, considering that nZVI will be eventually subjected *in situ* to a certain degree of surface oxidation, thus modifying the behavior of the NPs and their overall toxicity. To this end, Auffan et al. showed that polymorphous maghemite (γFe_2O_3), in which all the iron cations are in the trivalent state, have no apparent cytotoxicity toward *E. coli* between 7 and 700 mg/L (Auffan et al., 2008). Conversely, a dose-dependent toxicity appeared at concentrations higher than 700 mg/L for magnetite, whose unit cell can be represented as $(Fe^{3+})_8[Fe^{2.5+}]_{16}O_{32}$, and 70 mg/L for nZVI. The cytotoxic effects appear to be associated principally with an oxidative stress induced by the oxygenation of reduced Fe species (Fe^{II} and/or Fe^0), either within the nanoparticles lattice or following the release of Fe^{II} in solution.

Finally, more global studies were undertaken to assess the toxicity of iron nanoparticles toward indigenous bacterial communities from environmental matrices, rather than specific bacteria grown in the laboratory. Such insight is crucial to understand the potential synergy between nano- and bioremediation by determining, for example, if nZVI may have a biostimulatory effect on microorganisms participating in bioremediation. High Fe^0 concentrations (16.5 g/L) were deposited in both a sampled soil and groundwater contaminated by TCE and ClO_4^-, preliminarily bioaugmented with dechlorinating microorganisms (Rangan et al., 2020). It was observed that the particles promoted TCE abiotic reduction to ethene and ethane, while impairing microbiological TCE and ClO_4^- reduction. Conversely, a low concentration of aged-Fe^0 promoted microbiological TCE dechlorination to ethene while achieving a complete ClO_4^- reduction. Furthermore, Xiu et al. investigated the influence of nZVI on the community of indigenous dechlorinating microorganisms known as *Dehalococcoides* spp. that mediate the anaerobic remediation of trichloroethylene-contaminated sites (Xiu et al., 2010). Particles at a concentration of 1 g/L initially inhibited dechlorinating bacteria, although the populations were able to recover after about 300 hours. By contrast, methanogens (microorganisms that produce methane) were biostimulated. The authors concluded that nZVI caused the stimulation of H_2 production, which can be used as an electron donor by methanogens and dechlorinating bacteria.

These results are supported by other studies in which the addition of nZVI created significantly more reduced conditions and stimulated remediation efficiency of eubacteria towards TCE-

contaminated sites (Kirschling et al., 2010). It turns out that the dissolution of Fe^{2+} acts as a unique iron source for microbiota, promoting bacterial proliferation and bioremediation (Casals et al., 2014).

In comparison with bacteria, fungal species seem to display a much higher tolerance to nZVI toxicity, probably because fungal cell walls are composed of a very rigid assembly of mannoproteins and chitins, as well as α- and β- linked glucans. For instance, bare nZVI had no impact on the survival of the fungus *Aspergillus versicolor*, an ubiquitous contaminant of damp indoor environments, in concentrations up to 10 g/L (Diao and Yao, 2009). Further studies demonstrated that nZVI slightly altered *Saccharomyces cerevisiae* metabolism by reducing O_2 consumption by 44 % at 1 g/L, while no effect was observed with Fe_2O_3 nanoparticles (Otero-González et al., 2013). Moreover, Pawlett et al. (2013) showed that the soil biomass of Gram− bacteria and arbuscular mycorrhizal fungi, which are soil microorganisms interacting symbiotically with the roots of host plants, decreased under the effect of home-made CMC-nZVI (10 ± 5 nm) at a concentration of 270 µg Fe/g dry weigh soil (Pawlett et al., 2013). In a more recent and specific study, it was confirmed that nZVI could reduce the colonization of maize plant roots by arbuscular mycorrhizal fungi, thus having a counteractive effect on the symbiosis that may enhance plant resistance to pollutants such as metal(loid)s (Wu et al., 2018).

Table 6

1015 Significant results illustrating the *in vitro* toxicity studies conducted on bacterial and fungal species.

Abbreviations: CFU, colony forming unit; SEM, scanning electron microscopy; TEM, transmission electron microscopy; MALDI-TOF, Matrix Assisted Laser Desorption Ionization Time-Of-Flight mass spectrometry; D_h, hydrodynamic diameter.

Species tested (Gram, occurence)	NP characteristics	Experimental conditions	Incubation time	Analytical methods used	Impact	Ref.
Bacteria						
Agrobacterium sp. PH-08 (Gram−)	Home-made bare nZVI; carboxymethyl cellulose (CMC)-nZVI 80–120 nm	0.1 – 0.25 g/L; aerobic	1-6 h	CFU assay; TEM	Significant accumulation of bare nZVI onto cell surface; CMC coating reduced NZVI toxicity	(Zhou et al., 2014)
Agrobacterium sp. PH-08 (Gram−)	nZVI (NaBond, China) 36.3 ± 2.3 nm	0.1 – 1 g/L; aerobic	1-6 h	CFU assay; RT-qPCR; propidium iodine; TEM/SEM	0.1-log and 0.15-log inactivation after 6 h-exposure to 0.1 and 1 g/l nZVI, respectively	(Le et al., 2014)
Bacillus subtilis CB310 (Gram+)	nZVI (Toda Kogyo Corp., Japan) 50 nm–5 µm	1 g/L; 2 mM bicarbonate buffer; aerobic	1–4 h	CFU assay; TEM	Strong toxicity ~ 90 % inactivation after 4 h-exposure	(Chen et al., 2011)
Bacillus subtilis var niger (Gram+)	Home-made nZVI 20–30 nm	0.1-10 g/L; deionized water; aerobic	5 min	CFU assay; SEM	Strong bactericidal effect (80, 95 and 100 % inactivation at 0.1, 1 and 10 g/L nZVI, respectively); massive needle-shaped coating on cell surface	(Diao and Yao, 2009)
Escherichia coli ATCC 33876 (Gram−)	Commercial nZVI (Toda Kogyo Corp., Japan)*** with adsorbed polymers and natural organic matter	0.001–2 g/L; 5 mM bicarbonate buffer; aerobic and anaerobic condition	5-60 min	CFU assay; TEM	5.2-log inactivation for 28 % Fe(0) nZVI; <0.2-log inactivation with coated nZVI after 1h-exposure	(Li et al., 2010)
Escherichia coli ATCC 8739 (Gram−)	Home-made nZVI 10–80 nm	1.2–110 mg/L; 3 mM carbonate buffer; aerobic/anaerobic	60 min	Live/dead viability kit; oxidative stress assay; fluorescence	Disruption of cell membrane integrity and respiratory activity; higher	(Kim et al., 2010)

				microscopy	level of intracellular ROS under anaerobic conditions	
Escherichia coli BW25113 wildtype strain and mutant strains lacking genes that protect against oxidative stress (Gram−)	Commercial nZVI (Toda Kogyo Corp., Japan) 10-70 nm	1 g/L; 50 mM carbonate buffer; aerobic	5-60 min	CFU assay	More severe toxicity during exponential and decline growth phases; toxic effect is strain-dependent.	(Chaithawiwat et al., 2016b, 2016a)
Escherichia coli DH5α (Gram−)	Home-made nZVI coated with Pd, Cu, Ni and Pt 50-70 nm	10-500 mg/L; aerobic		CFU assay; oxidative stress assay; glutathione peroxidase (GPx) assay; TEM	Bactericidal effect in the order nZVI/Cu > nZVI > nZVI/Ni > nZVI/Pt > nZVI/Pd	(Kim et al., 2014)
Escherichia coli Qc1301 (Gram−)	Home-made nZVI (D_h 320±30 nm), Fe_3O_4 (380±40 nm), γFe_2O_3 (50±5 nm) NPs	7-700 mg/L; aerobic	1 h	CFU assay; TEM	Fe^{2+} or Fe(0) species increase toxicity for doses > 70 mg/L; no apparent toxicity of γFe_2O_3 NPs	(Auffan et al., 2008)
Escherichia coli ATCC 25922 (Gram−)	Home-made sulfide nZVI at different Fe/S ratios	10 mg/L; anaerobic	1 h	CFU assay; oxidative stress assay; TEM	2.95-log inactivation for nZVI *versus* 2.14-log for sulfide nZVI with the highest S content (molecular ratio Fe/S=10)	(Cheng et al., 2019)
Klebsiella oxytoca (Gram−) isolated from the nZVI-trated soil	nZVI (NanoFer 25S**) 80-120 nm	1-10 g/L; aerobic	0.2–24 h	CFU and liquid-to-plate assay, TEM/SEM, 2D-electrophoresis, MALDI-TOF	No bactericidal and negligible bacteriostatic effects; attachment of nZVI to cell surface without significant cell damage.	(Saccà et al., 2013)
Klebsiella planticola (Gram−) and *Bacillus nealsonii* (Gram+)	nZVI (NanoFer 25S**) < 50 nm	1–10 g/L; NaCl solution, aerobic	0.2–24 h	CFU assay, O_2 consumption, TEM/SEM	No effect on viability and activity of Gram− strain; 0.8-log inactivation for Gram+ strain	(Fajardo et al., 2012)
Pseudomonas putida G7 (Gram−, soil)	nZVI (NanoFer STAR*) 30-80 nm	1-10 µg/L; phosphate buffer; aerobic conditions	30 min	CFU assay, TEM, chemical-in-pond method, monitoring of swimming behavior	0.2-log cell inactivation; negative chemotactic response	(Ortega-Calvo et al., 2016)

Pseudomonas putida F1 (Gram−, soil)	nZVI (NanoFer 25S**) 5 ± 308 nm	0.1 – 5 g/L; M9G minimal medium; aerobic conditions	6 h	CFU assay, cell membrane composition analysis, TEM/SEM	2-4 log cell inactivation within 1 h; rebound in number of viable cells after prolonged exposure	(Kotchaplai et al., 2017)
Diphenyl ether degrading *Sphingomonas sp.* PH-07 (Gram−)	Home-made nZVI/Pd; necklace-like structure with 2 nm primary particles	0.05-0.1 g/L; MSM medium	130 h	Cell turbidity measurement; Bradford assay; SEM/TEM	Initial retardation in growth until 80 h before recovery	(Murugesan et al., 2011)
Fungi						
Aspergillus versicolor ATCC 26644 (Ascomycetous Fungi)	Home-made nZVI 20–30 nm	0.1-10 g/L; deionized water; aerobic	5 min	CFU assay; SEM	No toxic effect; yellow-brown coating observed on cell surface	(Diao and Yao, 2009)
Saccharomyces cerevisiae (Ascomycetous yeast)	nZVI 40–60 nm; Fe_2O_3 NPs 20-40 nm (Skyspring Nanomaterials Inc., USA)	0.1-1 g/L; aerobic	20 h	O_2 consumption; toxicity yeast assay; flow cytometry	44 % reduction of O_2 consumption at 1 g/L by nZVI; no toxic effect from Fe_2O_3 NPs	(Otero-González et al., 2013)
Arbuscular mycorrhizal (AM) fungal *Rhizophagus irregularis* - maize (*Zea mays* L.) plant association	Commercial nZVI 50-100 nm (Nano Iron)	0.5 % (w/w) in metal(oid)-contaminated soil	65 days	AM colonization assessment with trypan blue staining; SEM-EDS ; X-Ray diffraction	Decrease of mycorrizhal colonization and arbuscule abundance in the root system	(Wu et al., 2018)

* Commercial particles composed of 65-80 % Fe(0) and 20-35 % FeO/Fe_3O_4 (NANOIRON s.r.o., Czech Republic).

** Commercial poly(acrylic acid)-modified nZVI (NANOIRON s.r.o., Czech Republic).

1020 *** NPs synthesized by reduction of iron oxides using nitrogen gas.

6.1.2 Impact on other organisms

Data related to the adverse impact of NPs on aquatic and terrestrial organisms are limited, in comparison to the large amount of publications on bacteria. In all ecosystems (beyond bacteria), invertebrates and plants play a crucial role in the fate and transport of NPs through plant uptake and bioaccumulation. A pioneering work carried out by Barrena et al. studied the effects of model nanomaterials (Au, Ag and Fe_3O_4 NPs) on plants and microorganisms (Barrena et al., 2009). Germination, bioluminescent and anaerobic toxicity tests, conducted at particle concentrations up to 0.1 g/L, showed low or zero toxicity. Moreover, Garner and Keller showed that, on the basis of existing data, three nanomaterials seemed to be of concern: Ag, nZVI and ZnO (Garner and Keller, 2014). Of these, ZnO was the most problematic as it has been reported as toxic to all species tested (crustaceans, protozoans, microalga and phytoplankton). This impact was attributed to a severe pH variation, combined with the dissolution of the highly soluble ZnO material. In the case of nZVI, toxicity is generally observed at concentrations greater than 0.5-1 $mg.L^{-1}$ (El-Temsah and Joner, 2012), thus overlapping usual remediation concentrations, namely 1-10 $g.L^{-1}$. These inter-material differences can be attributed to extremely variable aggregation states and the analytical complexity of the tests performed which prevents drawing consensus from the results (Krug, 2014).

To date, the harmful effects of nZVI were observed in plant species, although there are many discrepancies among the published results. Libralato et al. reported no significant negative impact on aquatic plants known as macrophytes (*Lepidium sativum*, *Sinapis alba* and *Sorghum saccharatum*) up to concentrations used in field activities (34 g/L) (Libralato et al., 2016). By contrast, Ma et al. evaluated the phytotoxicity and accumulation of bare nZVI by two common plant species, cattail (*Typha latifolia*) and hybrid poplars (*Populous deltoids* × *Populous nigra*); nZVI exhibited a strong toxic effect on the former at high concentrations (> 200 mg/L) (Ma et al., 2013). The particles also significantly reduced the transpiration and growth of hybrid poplars, suggesting the biological effect to be species-dependent. However, in both cases, the upward transport of the particles from the roots to the shoots was minimal for both plant species, indicating an early aggregation once internalized in the roots.

Besides, other types of plants were investigated. El-Temsah et al. showed the impact of the synthesis routes of nZVI on barley and flax. It turns out that nZVI produced by precipitation with borohydride exhibited negative effects due to particle oxidation. Nevertheless, nZVI synthesized by gas phase reduction of iron oxides under an H_2 flow showed either a stimulatory effect or no effect at all (El-Temsah et al., 2016). Wang et al. studied the influence of nZVI on the germination and physiology of rice. Particles deposited in test soils at concentrations up to 1 g/L induced iron deficiency chlorosis (insufficient chlorophyll production) and inhibited seedlings growth (Wang et al., 2016).

Among soil organisms, earthworms play a key role in terrestrial ecosystems by recycling mineral nutrients and organic matter, and preserving soil structure. Two populations of earthworms (*Eisenia fetida* and *Lumbricus rubellus*) were exposed to nZVI. Regarding avoidance of treated soil fractions, weight changes, mortality and reproduction, both species were significantly affected by nZVI concentrations higher than 500 mg/kg (El-Temsah and Joner, 2012). Similarly, phyto- and zoo-planktons, which are organisms susceptible to be exposed downstream of nanoremediation sites, displayed decreasing population growth rates and increasing mortality in concentrations ranging from 0.5 to 3 mg/L (Keller et al., 2012). The authors suggest that toxicity stems partly from the oxidation products Fe^{2+}/Fe^{3+} released by the particles. This high sensitivity of marine organisms to nZVI was also shown by Yang et al. who observed an increased mortality and oxidative response with stabilized (rather than uncoated) nZVI of medaka fish larvae (*Oryzias latipes*) at concentrations as low

as 50-100 mg/L (Chen et al., 2013). The same group also demonstrated that, unlike CMC-nZVI and Fe^{2+}, Fe_3O_4 altered the fecundity and oocyte development in the ovaries of medaka adults (Yang et al., 2019).

Wider studies comprising multiple test species have also been conducted. Hjorth et al. assessed the ecotoxicity of commercially available iron-based nanoparticles, including iron oxide, nZVI and aluminosilicate loaded with Fe(III), on bacteria, algae, crustaceans, worms and plants (Hjorth et al., 2017). All materials, except ball milled nZVI, showed no toxicity when tested in concentrations up to 100 mg/L, which is the acceptable cutoff according to UE regulation. Another general study performed by Yoon et al. focused on the impact of different particle formulations – uncoated nZVI, nZVI coated with tetrapolyphosphate (TPP), carboxymethyl cellulose (CMC)-stabilized nZVI and bismuth (Bi)-doped nZVI – on multiple species including Gram− and Gram+ bacteria, plant (*Arabidopsis thaliana*), water flea (*Daphnia magna*) and earthworm (*Eisenia fetida*) (Yoon et al., 2018). Bi- and CMC-nZVI caused strong toxic effects on plant and water flea, while no impact was observed on earthworm, despite the high concentration employed (1 g/kg).

6.1.3 Human health implications

A major concern is that unreacted NPs, especially nZVI, can spread from the treatment areas and be harmful to human health. Based on the previous paragraphs, it turns out that nZVI have short lifetimes in the environment prior to inactivation (several weeks to months) and short distance shifts (< 100 meters) from the injection point.

Exposure pathways determine how NPs enter an organism, which is generally *via* the respiratory system, the gastrointestinal tract or the epidermis. Ingested or inhaled NPs can then cross biological barriers and migrate to various organs and tissues, such as the lungs, guts and skin (Boyes et al., 2017). Unlike larger particles, NPs can be taken up by cells. Following entry, NP toxicity generally depends either on their persistence in the organism or their clearance due to an immune response. From here it is hypothesized that they may translocate to secondary organs including spleen, kidneys and liver (Wu and Tang, 2018). Detrimental effects include oxidative stress, lipid peroxidation, genotoxicity, lung diseases, inflammation and pulmonary pathological changes leading to DNA mutations and major structural damages to mitochondria (Oberdörster et al., 2007). Beyond acute effects, concerns also rise about chronic toxicity, biomagnification and biopersistence of NPs, as well as the potentially increased uptake of pollutants facilitated by NPs (Giri, 2014).

In the case of iron-based NPs, it is assumed that exposure to nZVI by inhalation could result in the release of Fe(III), followed by oxidative damage due to the production of ferryl ions (Keenan and Sedlak, 2008). Also, *in vitro* studies have been performed to examine the response of central nervous system microglia to low concentrations (2-30 ppm) of nano-iron and nanomagnetite; it was shown that the particles were taken up into cells and subsequently induced oxidative stress (Wiesner et al., 2006). The authors underlined, though, that these *in vitro* responses reflected significantly higher exposures than expected. Furthermore, Fe_2O_3 NPs – as a potential end product deriving from redox reactions of nZVI – were internalized *in vitro* in human fibroblasts and caused a weak cytotoxicity (Auffan et al., 2006).

A secondary risk has been pointed out by Renn and Rocco concerning the potential vectorization of other contaminants (Trojan Horse effects) by NPs (Renn and Roco, 2006). Indeed, colloids have the ability to travel large distances in the environment, depending on the composition of groundwater and the hydrologic conditions. For instance, natural iron oxide NPs have been found several kilometers downstream from mining sites, demonstrating an ability to transport sorbed contaminants. In this regard, iron NP adsorption of contaminants, such as pesticides or heavy metals, may lead to their bioaccumulation and transfer in the food chain.

6.2 Other type of nanoparticles

Among the wide variety of materials used for nanoremediation, only a fraction has been investigated from a toxicological perspective. Apart from iron-based NPs, studies have focused mostly on carbon-based and metal oxide NPs, including TiO_2 (see (Theron et al., 2008) for review). Results were obtained mostly from *in vitro* studies and suggest that single- and multi-walled carbon nanotubes, as well as TiO_2 NPs, are toxic through the production of reactive oxygen species.

In addition, Auffan et al. pointed out that the chemical stability of metallic NPs at physiological redox conditions appears to be a condition for *in vitro* innocuity (Auffan et al., 2009). Indeed, chemically stable metallic NPs (*e.g.* γ-Fe_2O_3 NPs) did not exhibit *in vitro* cytotoxicity under physiological redox conditions, whereas metallic nanoparticles with a strong reductive power (*e.g.* Fe^0, Ag^0 and Cu^0 NPs) were cytotoxic and genotoxic towards biological targets. In the category of metal oxides, Pulido-Reyes et al. showed that cerium oxide NPs coated with polyvinylpyrrolidone (PVP) significantly increased the formation of reactive oxygen species in exposed cells, indicating that oxidative stress is an important toxicity mechanism for NPs (Pulido-Reyes et al., 2019). Additionally, Schultz et al. observed a similar behavior between nZVI and silver-based nanoparticles: aging transformations reduced the bactericidal effect of pristine and sulfidized nano-Ag in media with organic matter, although the release of cationic silver through dissolution could not account entirely for the observed toxicity (Schultz et al., 2018).

7. Perspectives

Bardos et al. have recently identified around 100 “in the field” nanoremediation projects documented worldwide (Bardos et al., 2018). However, the majority of other remediation and water purification studies involving NPs remains at a bench scale proof of concept stage (Qu et al., 2013). So far, systems such as spiked soils, which were proven to be successfully remediated, subsequently failed to perform well in field soils because real contaminated soils are much more complex (Kuppusamy et al., 2017). As said before, the mobility of either natural or synthetic NPs in an environmental matrix will strongly depend on whether the particles remain completely dispersed, aggregate and settle, or form mobile nanoclusters. Having realized the limited soil mobility and deliverability of bare nZVI (Crane and Scott, 2012), researchers are currently seeking more effective stabilization techniques and more deliverable nZVI, also opening the way for the development of alternative materials such as titanium and cerium-based NPs.

These purely investigative factors are intertwined with out-of-the-lab parameters, thus slowing down the development of nanoremediation. Mueller et al. described in a short overview the practical experience with nZVI applications in Europe, and compared it to the situation in the USA (Mueller et al., 2012). Until 2012 in Europe, only three full-scale nZVI-based remediation treatments – solely targeting groundwater – had been carried out, while it was already an established methodology in the USA, both for groundwater and soils. It seems that the scarcity of nZVI applications in Europe is not only due to technical reasons, but rather based on economic constraints and a precautionary approach. For instance, bimetallic Fe-Ni particles are not used in Europe because there are concerns regarding the toxicity of the catalysts (*e.g.* Ni is considered a hazardous substance under the European Union Water Framework Directive).

In this context, several issues need to be addressed:

(i) The acceptance by the authorities, *i.e.* the determination of specific regulations through evaluation by governmental agencies, and by society (Bardos et al., 2018).

(ii) The costs associated with the technology, since there is no generic cost calculation for nanoremediation which relies heavily on site-specific factors.
(iii) The lack of long-term experience with this technology, associated with the difficulties in securing funding for research on the field scale.
(iv) The concerns about potential impact on human health and ecotoxicological effects.

On the basis of several governmental position papers (*e.g.* from the Royal Society, the Québec commission, the US EPA), Karn et al. found in 2009 that nZVI particles intended for remediation are generally looked on as more beneficial than harmful, although more research on its environmental effects are required (Karn et al., 2009). However, a contradictory field test using nZVI was carried out at a German site contaminated with chlorinated hydrocarbons by the Federal Institute for Geoscience and Natural Resources (Houben, G. et al., 2006). Particle injection caused significant changes in the redox chemistry of the groundwater, while other physicochemical and hydrochemical parameters remained unaffected. The limited penetration depth and lateral dispersion of the nZVI resulted in the cleanup of a small portion of the test site. The authors reported technical difficulties to disseminate the NPs belowground, concluding that nZVI-associated remediation was not yet ready for large scale applications; the institute consequently dropped its activities related to nZVI.

The potential environmental and health risks associated with this next generation technology have just been realized (Keller and Lazareva, 2014). To prevent negative effects, a proper evaluation, including full-scale ecosystem-wide studies, of these nanomaterials should be undertaken before nanoremediation can be used on a mass scale. Some corporations have been reluctant to apply this technology because the uncertainties of the technology could lead to litigation cases. For example, DuPont Chemicals published in 2007 a nanomaterials risk assessment work sheet and decided to postpone further development of nZVI at its sites. The company representatives stated that issues concerning fate and transport should be more thoroughly researched since there were too many uncertainties regarding nZVI potential environmental risks (DuPont Chemicals, 2007).

If the precautionary principle is regularly invoked, one should not forget that the environmental marketplace is driven and channeled by regulations and laws, thus steering funding policies for controlled pilot and field projects. Additionally, Choi et al. commented that it is very important to gather information about the toxicity of NPs in order to have proper regulation plans, although they estimated that, for the USA alone, costs for testing existing NPs would range from US$ 249 million (based on optimistic assumptions about NP hazards) to US$ 1.18 billion (precautionary approach) . Also, the time taken to complete testing is likely to be very high (34-53 years), if all existing nano-candidates are to be thoroughly tested. Of course, factors such as the maturation of the field, the understanding of the mechanisms involved and common sense will significantly shorten these timeframes, and reduce the cost and efforts to properly regulate nanomaterials (Choi et al., 2009).

8. Conclusion

The use of nanoparticles is not exempt of limitations, *e.g.* proneness to rapid passivation, easy aggregation, susceptibility to geochemical conditions and possible environmental and human health threats, if not applied properly. The case of nZVI presents an interesting example whereby the promises of this emerging technology may be partially unfulfilled, given the potential risks and concerns related to its *in situ* long-term effectiveness, as well as unknown downstream consequences of its use. One must balance the existing risks of the contamination at a given site with potential risks of nanoremediation, including its unknown, long-term consequences and uncertainties.

Regarding potential toxic responses, it is important, first of all, to understand the underlying specific "mode of action" of a given nanomaterial. Second, it is recommended that additional research activities focus on the potential for NPs to migrate into the matrices through the use of specific coatings. Third, more nanokinetic studies – based on their pharmacokinetic counterparts – should be undertaken to finely understand and adjust the physicochemical transformations governing the fate of NPs. This could enable scientists, researchers and developers to understand and predict the behavior of these novel materials in the environment. In this regard, a synergy between academic studies and more advanced lab- and field-scale experiments is desirable, although the economic reality and private stakes cannot obviously be ignored. Even though several companies are working with nZVI for the remediation of contaminated soils and groundwater, there are still questions to be answered not only by researchers, but also by governments to make it a fully reliable remediation technology. This growing awareness should be accompanied by the development of other promising nanomaterials exhibiting new and complementary features over current remediation approaches.

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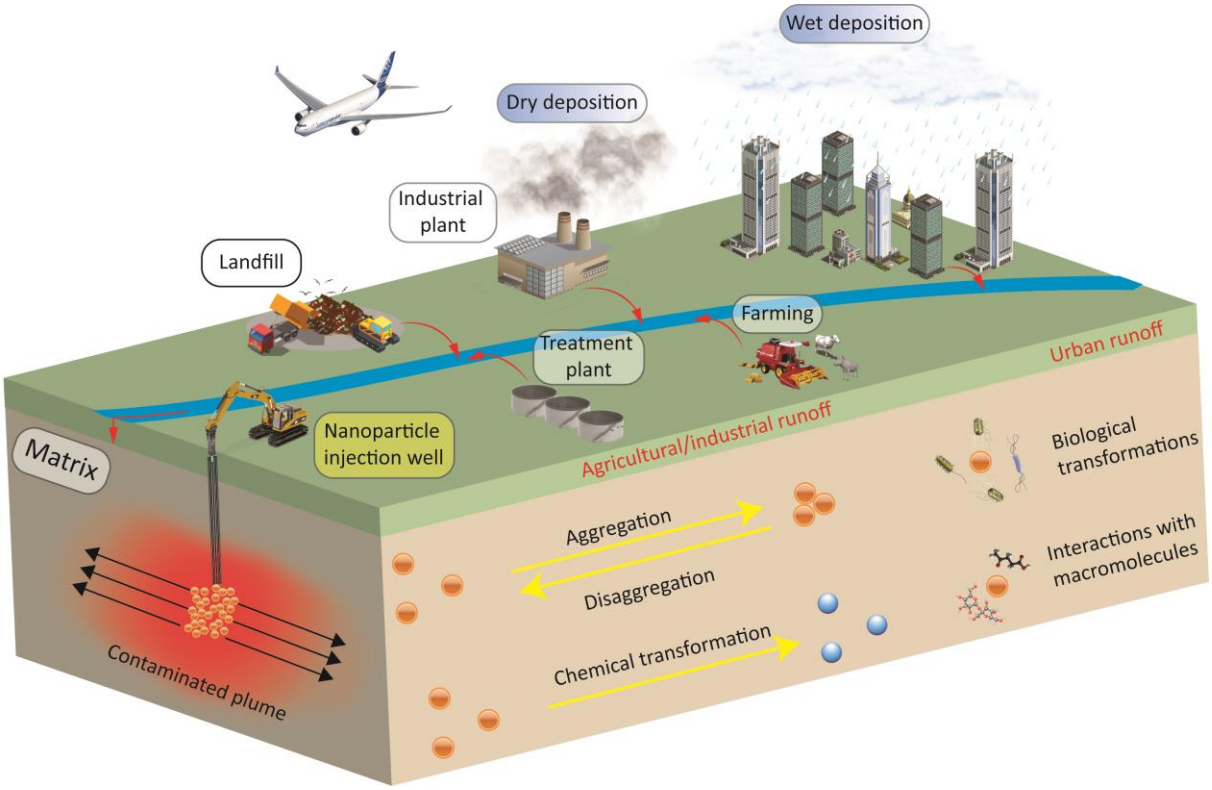
Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Graphical abstract



Highlights

- Anthropogenic pollution has continuously increased since the industrial revolution.
- Nanoparticles can provide solutions to *in situ* cleanup challenges.
- Nano-objects are increasingly being deployed in the field since the 2000s.
- Their use is not exempt of limitations (aggregation, human health risks).
- Their slow development in Europe is also due to economic motives and regulatory issues.
- Questions concerning toxicity and migration into the matrices need to be answered.

Declaration of interests

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☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: