

# Status of Nanoremediation and its potential for future deployment: Risk-benefit and benchmarking appraisals

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## Abstract

NanoRem (Taking Nanotechnological Remediation Processes from Lab Scale to End User Applications for the Restoration of a Clean Environment) was a research project, funded through the European Commission's Seventh Framework Programme, which focuses on facilitating practical, safe, economic, and exploitable nanotechnology for *in situ* remediation of polluted soil and groundwater, which closed in January 2017. This paper describes the status of the nanoremediation implementation and future opportunities for deployment based on risk-benefit appraisal and benchmarking undertaken in the NanoRem Project.

As of November 2016, NanoRem identified 100 deployments of nanoremediation in the field. While the majority of these are pilot scale deployments, there are a number of large scale deployments over the last five to ten years. Most applications have been for plume control (i.e., pathway management in groundwater), but a number of source control measures appear to have taken place.

Nanoremediation has been most frequently applied to problems of chlorinated solvents and metals (such as chromium VI).

The perception of risk-benefit balance for nanoremediation has shifted as the NanoRem project has proceeded. Niche benefits are now more strongly recognized, and some (if not most) of the concerns, for example relating to environmental risks of nanoremediation deployment, prevalent when the project was proposed and initiated have been addressed. Indeed, these now appear overstated. However, it appears to remain the case that in some jurisdictions the use of nanoparticles (NPs) remains less attractive owing to regulatory concerns and/or a lack of awareness, meaning that regulators may demand additional verification measures compared to technologies with which they have a greater level of comfort.

## 1 Introduction

*In situ* remediation techniques (exploiting biological, chemical, physical stabilization, and/or thermal processes within the subsurface) are being increasingly used to avoid excavation of materials or surface treatment of groundwater from “pump and treat” projects.

*Nanoremediation* describes the use of nanoparticles (NPs) in the treatment of contaminated groundwater and soil. Depending on the properties of different particles, nanoremediation processes generally involve reduction, oxidation, sorption, or their combination (Lee *et al.*, 2014). NPs are usually defined as particles with one or more dimensions of less than 100 nanometers (nm) (Rauscher *et al.*, 2014). In practice, nanoremediation may apply to particles which are larger, for example composites, but which include activities at nanoscale dimensions such as NanoREM’s Carbolron® UFZ, Leipzig, Germany). NPs used in remediation are primarily metals or metal oxides, most frequently nanoscale zerovalent iron (nZVI). They may be modified in various ways to improve their performance, for example inclusion of a catalyst (often palladium), use of coatings or modifiers, or emplacement on other materials such as activated carbon or zeolites (for iron oxides). They are generally applied *in situ* via various injection methods, which may include the use of viscosity control agents or other materials to facilitate targeted emplacement of NPs in the subsurface. The use of NPs potentially extends the range of available *in situ* remediation technologies, and it may offer particular benefits in some applications (O’Carroll *et al.*, 2013; Bardos *et al.*, 2011).

As a result of their size, NPs can have markedly different physical and chemical properties compared to their micro-sized counterparts, potentially enabling them to be utilized for novel purposes, including remediation. To date, the most widely used NP in remediation has been nZVI. While the possibility of unique characteristics gives nZVI promise for beneficial applications, it is simultaneously a cause of concern, as there is a degree of uncertainty with regards to particle behavior, fate, and toxicity. As produced, most nZVI falls into the 10 to 100 nm size range (O’Carroll *et al.*, 2013; Müller & Nowack 2010; Karn *et al.*, 2009; Nurmi *et al.*, 2005), although it tends to agglomerate to form larger particles.

The first documented field trial of nZVI, in 2000, involved treatment of trichloroethylene in groundwater at a manufacturing site in Trenton, New Jersey, USA (Elliott & Zhang, 2001). Several commentators anticipated that nZVI technology would take off rapidly because of its perceived benefits such as rapid and complete contaminant degradation. In 2007, a European report forecast that the 2010 world market for environmental nanotechnologies would be around \$6 billion (Rickerby & Morrison,

2007). In practice, this market was not achieved. However, subsequent uptake of the technology has been relatively slow compared to other contemporary process-based technologies.

NanoRem was a large research project, funded through the European Commission's Framework 7 research programme. The NanoRem project focused on facilitating practical, safe, economic, and exploitable nanotechnology for *in situ* remediation. This was undertaken in parallel with developing a comprehensive understanding of the environmental risk-benefit for the use of NPs, market demand, overall sustainability, and stakeholder perceptions. The project was designed to unlock the potential of nanoremediation processes from laboratory scale to end user applications and to support both the appropriate use of nanotechnology in restoring land and water resources and the development of the knowledge-based economy at a world leading level for the benefit of a wide range of users in the EU environmental sector. It has provided a substantial platform of information and guidance, including a series of 12 Technical Bulletins ([www.nanorem.eu/Displaynews.aspx?ID=938](http://www.nanorem.eu/Displaynews.aspx?ID=938)). Comprehensive project outcomes are publicly available via an on-line toolbox at <http://www.nanorem.eu/toolbox/index.aspx#TB1>.

This paper presents results from the NanoRem project on the current status of the nanoremediation implementation and on assessment and opportunities for nanoremediation deployment. Current status of the nanoremediation was undertaken from literature review and field cases tested in the NanoRem Project. Assessment of nanoremediation deployment and future opportunities for its deployment were carried out through risk-benefit analysis and benchmarking of NanoRem with respect to in-situ bioremediation and conventional in-situ chemical reduction using macro-scale iron.

This paper reports on three aspects of NanoRem's work:

1. Identification of field-based deployments of nanoremediation, including six deployments by NanoRem listed in Exhibit 1 (NanoRem 207a-f);
2. A risk-benefit appraisal for nanoremediation use; and,
3. Benchmarking the performance of nanoremediation against its two main market competitors: more conventional approaches to *in situ* chemical reduction (ISCR) and *in situ* bioremediation (ISBR).

**Exhibit 1** NanoRem field-based pilot tests

Site Name	Spolchemie I	Spolchemie II	Solvay	Balassagyarmat	Neot Hovav	Nitrastur
Site Primary Investigator	AQUATEST	AQUATEST	Solvay	Golder	Ben Gurion University of the Negev	Tecnalia
Country	Czech Republic	Czech Republic	Switzerland	Hungary	Israel	Spain
Current use	Industry	Industry	Industrial brown-field	Brownfield	Industry	Brownfield
Specification of contamination (source/plume)	Dissolved plume	Residual phase and dissolved plume	Pooled phase and dissolved plume	Dissolved plume	Non-aqueous phase and plume in fractures	Anthropogenic backfill containing heavy metals
Main contaminant(s)	Chlorinated hydrocarbons	BTEX (mainly toluene and xylenes), styrene	Chlorinated hydrocarbons	PCE, TCE, DCE	TCE, cis-DCE, toluene	As, Pb, Zn, Cu, Ba, Cd
Type of Aquifer	Porous, unconfined	Porous, unconfined	Porous, unconfined	Porous, unconfined	Fractured	Porous, unconfined
Hydraulic conductivity	$10^{-6}$ to $10^{-4}$ m/s	$10^{-6}$ to $10^{-4}$ m/s	$2 \times 10^{-5}$ to $8 \times 10^{-3}$ m/s	$2 \times 10^{-8}$ to $5 \times 10^{-3}$ m/s	n/a	$10^{-5}$ to $2 \times 10^{-4}$ m/s
Seepage velocity	0.2 m/d	0.9 m/d	5-20 m/d	0.3 m/d	not available	1 m/d
NP used	NANOFER 25S/ NANOFER STAR	Nano-Goethite	FerMEG12	Carbo-Iron®	Carbo-Iron®	NANOFER STAR
NP provided by	NANO IRON, s.r.o.	University Duisburg Essen	UVR-FIA GmbH	SciDre GmbH	UFZ	NANO IRON, s.r.o.
Mass of NP injected	200 kg / 300 kg	300 kg	500 kg	176.8 kg	5 kg	250 kg
Injection System	Direct Push	Direct Push	Wells (with packers)	Direct Push	Wells (with packers)	Wells (with packers)

**Abbreviations:** As – arsenic; Ba – barium; Cd – cadmium; Cu – copper; Pb – lead; Zn – zinc; m/d = meters per day

## 2 Status of field based tests and applications of nanoremediation

In 2011, a review of nanoremediation for the UK Government identified 58 deployments of nZVI in the field from pilot tests to commercial applications (Bardos *et al.*, 2011). By the end of November 2016 NanoRem extended this listing to approximately 100 field based deployments, taking into account multiple deployments on one site. These are listed in the Supplemental Materials. The Supplemental Materials only cite deployment where at least some public domain documentation was found. However, it should be considered an indicative rather than an exhaustive listing. Moreover, anecdotal information suggests further deployments have taken place, even one or two pilot tests in the UK where there is a “voluntary” moratorium on nanoremediation in place.

The field deployments are distributed across 92 sites as follows: Belgium, 1 site; Canada 4; Czech Republic 12; Denmark 2; France 2; Germany 7; Hungary 4; Israel 2; Italy 1; the Netherlands 1; Portugal 2; Spain 2; Switzerland 1; Taiwan 1; and USA 49. This listing includes the NanoRem pilot sites. Sixteen of these sites received “full” scale nanoremediation deployments. The remainder were either pilot / field tests or no information on scale was available. Treatments at 79 sites were directed at groundwater, including 18 where treatment of aquifer materials or “soil” is also mentioned. Treatments at three sites appear to have been directed at “soil only”. There is no information on media treated for nine of the sites. The vast majority of deployments are of nZVI, typically modified variants. Of the nZVI deployments 18 were bimetallic particles doped with palladium, 4 were in emulsions, 3 were stabilized in carbon, and 4 on minerals. Three recent applications of nanogoethite were also identified.

Nanoremediation at 76 of these sites treated dense nonaqueous phase liquid (DNAPL) (chlorinated solvents). In nine of these cases other contaminants were also mentioned including perchlorate, polychlorinated biphenyls (PCBs), petroleum hydrocarbons, and metals. Metals treatment was the focus for six sites, in particular hexavalent chromium (Cr[VI]), with it also occurring in two of the mixed contamination sites. For the handful of remaining sites, treatments were aimed at PCBs or pesticides, with one nanogoethite application targeted for light nonaqueous phase liquid (LNAPL) contamination. The contaminant(s) was not specified at two sites. Other contaminants recorded at test sites include Freon, phthalates, polycyclic aromatic hydrocarbons (PAHs), and nitrate.

Information on risk management application is not provided except in a few cases. However, 19 of these applications (4 at “full” scale) appeared to include DNAPL as a contaminant source, or at least a residual source, on the assumption that reported DNAPL concentrations exceeding 10,000 micrograms per liter ( $\mu\text{g/L}$ ) are likely indicative of a source / residual source. The remainder are more likely to be pathway (plume) management applications.

The most recent deployments use more advanced nanoparticle products produced in Europe (and tested by NanoRem) as US and Japanese production and supply has diminished, as a result of low levels of use. Where information has been provided, applications of <10 kg of NPs are recorded for 9 sites; 10 to <100 kg for 16 sites; 100 to <1,000 kg for 27 sites; and >1,000 kg for 11 sites. No information on the mass of NPs deployed is available for the other sites. The principle application approaches are gravity / infiltration based methods or direct push / injection under pressure. Application via fracturing was also used in a few instances.

While the number of deployments has certainly increased over the last five years, the total number of deployments, particularly in a commercial context, remains relatively low compared to conventional ISCR and ISBR. There are potentially two inter-related sets of reasons for this: the first is the level of benefit for using nanoremediation, compared with the level of risk; and also how nanoremediation benchmarks against conventional ISCR and ISBR. The remainder of this paper provides an updated risk-benefit appraisal and benchmarking based on the work of the NanoRem project.

### 3 Risk-Benefit Appraisal for NanoRem technologies

#### 3.1 Technology benefits

This section focuses on how nanoremediation may also offer specific and particular benefits in some applications. It is based on two types of information: (1) literature data published on the use of NPs for contaminated land remediation up to 2016 and (2) NanoRem Project results (including laboratory testing and field trial results from the sites listed in Exhibit 1). These include benefits related to **the range of treatable contaminants**, **the speed** by which they can be treated, **the range of environmental conditions** under which nanoremediation can perform, **the potential for source treatment**, and **potential synergies with other treatments**. This section focuses on nZVI for which the best evidence base exists; however, other NPs – especially those tested by NanoRem – are discussed wherever possible.

##### 3.1.1 Extended range of treatable contaminants

For the most part, nanoremediation based on nZVI has been used to treat chlorinated solvent contamination and trace element contamination, in particular CrVI (see Supplemental Materials). Laboratory-scale tests from the technical literature indicate that nZVI could treat a wide range of contaminants, although relatively few of these have been subjected to field-based treatability studies. Potentially treatable contaminants include: PAHs, complex chlorinated aromatic compounds (such as PCBs), pentachlorophenol (PCP), and the chlorinated benzenes (Cheng *et al.*, 2010, Chang *et al.*, 2005, 2007, 200p; Zhu & Lim 2007; Lowry & Johnson 2004; Xu & Zhang, 2000). Chang *et al.* reported two studies focusing on nZVI remediation of soils impacted by PAHs, particularly pyrene, which appeared to demonstrate declining contaminant concentrations over time and as a function of nZVI dose, but which did not identify specific degradation mechanisms (Chang *et al.*, 2005, 2007, 2009). nZVI has also been considered as a treatment for radionuclides such as radium and uranium (Burghardt & Kassahun 2005), with several laboratory studies suggesting this to be feasible (Scott *et al.*, 2011; Dickinson & Scott, 2010). Fan *et al.* (2013) demonstrated the ability of sulfidated nZVI to reductively sequester pertechnetate for the remediation of technetium-contaminated groundwater. Nanoscale / micro-scale metallic particles have also been shown at laboratory-scale to be a potential remediation technique for energetic (explosive) materials (Geiger *et al.*, 2009; Naja *et al.*, 2008). Doping nZVI with metals such as palladium further improves its reactivity and the range of applicable contaminants by introducing extended catalytic properties (Cook, 2009; Sirk *et al.*, 2009; Quinn *et al.*, 2009; Kim *et al.*, 2008; Saleh *et al.*, 2007; Elliott & Zhang, 2001). In addition, according to the Kharisov's review (Kharisov, 2012), common environmental contaminants that can be transformed by nZVI, supported and alloys nZVI, iron oxide, and FeOOH) may include: chlorinated and brominated methanes, pesticides (DDT, lindane), organic dyes (Orange II, Chrysoidine, Tropaeolin O, Acid Orange, Acid Red), heavy metal ions (Hg<sup>2+</sup>, Ni<sup>2+</sup>, Ag<sup>+</sup>, Cd<sup>2+</sup>, Cr[VI]), dioxins, other organic contaminants (N-

nitrosodimethylamine, dinitrotoluene, trinitrotoluene (TNT), RDX [hexahydro-1,3,5-trinitro-1,3,5-triazine] and inorganic anions [ $\text{Cr}_2\text{O}_7^{2-}$ ,  $\text{AsO}_4^{3-}$ ,  $\text{ClO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ ]. Laboratory results offer unprecedented details about the intra-particle reaction mechanisms and demonstrate intrinsic advantages of nZVI for arsenic encapsulation, treatment, and remediation (Ling & Zhang, 2014; Yan *et al.*, 2012).

At field-scale, most deployments of nZVI have focused on the degradation of chlorinated solvents, although pilot studies have also demonstrated successful treatment of benzene, toluene, ethylbenzene, and xylenes (BTEX), perchlorates, CR(VI), diesel fuel, PCBs, and pesticides. O'Carroll *et al.* (2013) detail the chemical processes involved in the treatment of chlorinated solvents and various metals by nZVI. A review of approximately 100 field deployments (see Supplemental Materials) indicates that nZVI was used to treat contaminants such as other halogenated organic compounds (methylene chloride, 1,2-dichloropropane, 1,2-dichloroethane, vinyl chloride, trichloroethane, hexachlorobutadiene), PAHs (benzo[a]anthracene), (bis[2-ethylhexyl]phthalate, perchlorate, Freon,  $\text{NO}_3$ ), PCBs and metals (Cr, Ni).

NanoRem work has included the improvement of nZVI performance (e.g., via the use of air stable particles (NanoRem, 2017g) and a range of more novel NP types that potentially extend the range of problems treatable by nanoremediation. It has tested the use of nano-goethite (iron oxide) to stimulate ISBR (oxidation) of benzene and toluene group contaminants. This has shown significant potential at laboratory scale, although pilot-scale test outcomes are less clear cut (NanoRem, 2017b; NanoRem, 2017g). NanoRem has also carried out laboratory and field-based tests of a novel combined particle consisting of nZVI sorbed to activated carbon (Carbo-Iron<sup>TM</sup>). The rationale for this nanoparticle is to improve the persistence of the nano-scale activity and provide a trap and treat capability. NanoRem conducted field tests related to chlorinated solvents (NanoRem 2017d). In addition, NanoRem performed laboratory-scale tests using several other NP types, including:

- “Trap-Ox” Fe-zeolites, microporous aluminosilicates, loaded with FeII/III ions by ion exchange, as an assist for Fenton’s-based *in situ* chemical oxidation applications.
- The use of bionanomagnetite for nanoremediation of chlorinated solvents and trace elements, as a “green” alternative to chemical synthesis routes (Watts *et al.*, 2015).

### 3.1.2 Improving the speed of contaminant destruction

The speed with which contaminants can be degraded or stabilized by NPs can be substantially increased over conventional *in situ* saturated zone remediation technologies because a greater amount of iron is readily available for reaction (e.g., Müller and Nowack, 2010; Li *et al.*, 2008). This may bring wider benefits. Karn *et al.* (2009) suggest that shortened timescales (e.g., compared with pump and treat) not only reduce costs but also reduce the time that workers are exposed to a contaminated site during its treatment. NanoRem laboratory and field results showed that activation process has improved speed and kinetics for an air stable nZVI, NANOFER STAR.

### 3.1.3 Improving the extent of contaminant destruction

A further claim made for nZVI use in remediation is that it offers the potential for rapid and complete treatment without the generation of toxic intermediate breakdown products, or that it generates more benign reaction products compared with ISBR (Bezbaruah, 2009; Nurmi *et al.*, 2005). Avoiding

toxic intermediates could be a major process benefit, if it is achievable in the field, particularly for sites where the pathway to potential receptors is relatively short.

Bench-scale studies indicate that, in the presence of nZVI, tetrachloroethene (PCE) is degraded fully to ethane, ethene, or other light non-chlorinated hydrocarbons, without the build-up of toxic intermediates (Taghavy *et al.*, 2010; Wang *et al.*, 2010; Henn & Waddill 2006; Gavaskar *et al.*, 2005). This has been compared with the field-scale performance of ISBR for treating chlorinated solvents, which can proceed to non-toxic products as well, but where there are instances of the accumulation of lesser chlorinated daughter products including the dichloroethenes (mainly cis-1,2-DCE, trans-1,2-DCE) and/or vinyl chloride (VC) (Interstate Technology and Regulatory Council [ITRC], 2008). The reasons for DCE accumulation are typically site specific; there is a body of evidence suggesting that in some cases it is because the local microbial community lacks a competent DCE degrader. This issue has been successfully remedied in a number of cases by inoculation of the aquifer with *Dehalococcoides* (ITRC, 2008). Overall, there are few reports of intermediate product accumulation during nZVI treatment of chlorinated solvents, although de Boer *et al.*, (2010) reported that there may be some, short-lived production of toxic intermediates such as VC. Available evidence, therefore, supports a view that process intermediates may accumulate for both ISBR treatments and nZVI applications in the field, depending on site-specific circumstances (and the sufficiency of added nZVI). However, it is also possible that the process intermediates observed during nZVI use in the field may be a consequence of biological processes rather than abiotic processes. Furthermore, the theoretical outcome remains one of complete contaminant destruction.

NanoRem field tests results on observation of degradation products confirmed existing knowledge from previous work, a rapid and total degradation of chlorinated compounds in ethane and, in some cases, the presence of cis-DCE, which may be due to secondary biological processes (NanoRem 2017a – f).

#### **3.1.4 Extended range of environmental conditions**

nZVI has been shown to be effective across a broad range of soil pHs, temperatures, and nutrient levels (Kharisov, 2012). Nanoremediation would also not be subject to conditions that might be inhibitory to biological processes. For example, as yet unpublished NanoRem laboratory-scale results showed that biomagnetite NP had a high resistance to inhospitable aquifer conditions (e.g., pH). Biomagnetites are considered to be reactive against a wide range of environmental conditions and at a range of pH values. Very high degradation rates were observed for biomagnetite and Pd-biomagnetite ( $K_{obs}$  respectively of  $6.6 \times 10^{-2}$  per hour [h] and 1.5/h) for the treatment of Cr(VI) under very basic conditions (pH=12).

#### **3.1.5 Potential for providing source term treatment capability**

There are limitations to the effectiveness of any *in situ* approach to source removal / destruction. However, nZVI deployment may be effective for treating small source areas, for example, what are often termed as secondary sources. Secondary sources may be used to describe two types of sources: (1) free product that has migrated away from the original source (Deeb *et al.*, 2014); and, (2) more colloquially, small product sources on a contaminated site. Summary information from the U.S. Environmental Protection Agency (EPA, Federal Remediation Technologies Roundtable [FRTR], 2006) describe a pilot application of bimetallic NPs (platinum-doped nZVI; referred to as “BNP”) for dis-

persed sources of chlorinated solvents, which achieved rapid treatment of dissolved phase chlorinated solvents at some, but not all, well locations.

Some of NanoRem's laboratory findings may be relevant for promoting source treatment. They include the following:

(1) inclusion of surfactant in the NP suspension to assist accessibility to DNAPL;

(2) Carbo-Iron® has advantages for free-phase DNAPLs as the Carbo-Iron® is hydrophobic. The carbon fraction sorbs DNAPL; therefore, making it accessible to the iron. The possibility of Carbo-Iron® entering the NAPL phase has not yet been observed for methodological reasons, but it certainly collects at the phase boundary; and:

(3) The potential for providing source treatment is highly dependent on the existing deployment techniques and their ability to deliver NPs in the contaminated zone. The aboveground preparation of the suspension appears to be more critical to success than the actual injection approach. There is a need for good information about the permeability of the subsurface to use the right technology to inject the material. Injection into low permeability layers is not feasible.

Regarding the NanoRem testing sites, three of the six test sites targeted some types of source treatment (secondary or residual):

- At the Spolchemie I site, Usti nad Labem, Czech Republic, a DNAPL secondary source area removal was targeted, injection of NANO FER 25S and NANO FER STAR (NanoRem, 2017a).
- At the Spolchemie II site, Usti nad Labem, Czech Republic, LNAPL contamination, including toluene, was targeted, mainly in the plume, but including small amounts of residual phase, using iron oxide (Nano-Goethite) NPs (NanoRem, 2017b).
- At the Solvay site, Switzerland, the initial aim was to treat the plume and eventually inject iron in a DNAPL secondary source zone where the contaminants are present in pools, as residual phase and at the bottom of the aquifer, using milled nZVI particles, FerMEG12 (NanoRem 2017c).

The degree of contamination treatment success of the NanoRem test sites (listed in Exhibit 1) varied depending on the site and the type of NPs injected. These were pilot scale treatments so effects were localised and limited in duration. In all cases some reduction in target contaminant levels was found. At the Spolchemie site I, the second NANO FER STAR injection showed efficient degradation of PCE. At the Solvay site, even if the concentrations of contaminants found in the test area are very high compared to the nearest extraction well, it was concluded that a successful treatment of the identified secondary source will only have a small impact on the concentration of contaminants in the extraction well. The working hypothesis that back diffusion of the contaminants from the clay formation is responsible for the groundwater contamination, could not be verified as free phase product was present. At the Spolchemie II site, the contaminant concentrations are still very high due to a slow bioremediation process, especially under anoxic/anaerobic (iron reducing) conditions.

### **3.1.6 Synergy and enhancement effect**

A number of emerging NP approaches include combined treatments including nZVI with other treatments, for example, thermal destruction (Varanasi *et al.*, 2007), electrokinetic treatments (Gomez *et al.*, 2015a, 2015 b), and ISBR (Bruton *et al.*, 2015). Of these combined ISBR and ISCR is the most developed, and the synergy between nZVI addition and supporting biological processes of dehalorespiration is a significant opportunity for nZVI deployment.

Various studies suggest that nZVI may be suitable for deployment in conjunction with other remediation technologies, with some studies even demonstrating a synergistic effect. For example, Jiamjitrpanich *et al.* (2012) examined the compatibility of nZVI with phytoremediation techniques for treating TNT in soil, where TNT contaminated soil was treated with hyperaccumulator plants and nZVI applications, as both single and combined treatments. Results suggested TNT removal was highest for treatments involving a combination of nZVI and hyperaccumulator plants. Similarly, Baiget *et al.* (2013) found nZVI used in combination with a microbial bioremediator, *Shewanella putrefaciens*, produced synergistic effects for the removal of uranium from contaminated effluent.

Interestingly, field and laboratory bench-scale observations indicate that nZVI use is synergistic and stimulatory for *in situ* anaerobic biodegradation of chlorinated solvents by dehalorespiration. Laboratory studies indicate that nZVI application does not appear to be inhibitory to (and may even be stimulatory for) biological reductive dechlorination associated with water-derived cathodic H<sub>2</sub> production during its anaerobic corrosion (Comba *et al.*, 2011; Kirschling *et al.*, 2010; Xiu *et al.*, 2010). Kuang *et al.* (2013) found corroborating results supporting this theory, demonstrating that both nZVI and Ni/Fe composite NPs increased the biodegradation of phenol by *Bacillus fusiformis* at pH 6 and 8; nZVI was also demonstrated to increase biodegradation at low pH (pH 3). These laboratory findings are consistent with observations during applications of nZVI in the field, where biological reductive dechlorination continues or is stimulated (e.g., He *et al.*, 2010; Kocur *et al.*, 2015). Indeed, Lacinová *et al.* (2013) showed that in field tests sequentially combining nZVI and *in situ* biostimulation achieved greater reduction in chlorinated solvents in a contaminated aquifer (76 percent compared to 48 percent for nZVI alone). Koeniga (2016) proposed a unique treatment train combining nZVI and organochlorine respiring bacteria (ORB) which, when applied at appropriate doses, can potentially treat a wider range of chlorinated aliphatic hydrocarbons (CAHs) than each individual remedy. Combining two Cr(VI) geofixation methods – chemical reduction by nZVI and subsequent biotic reduction supported by whey – resulted in a further and long-term decrease in the Cr(VI) and chlorinated solvents concentrations in groundwater (Nemecek, 2015, 2016).

NanoRem bench-scale results suggest that the carbon in the Carbo-Iron® may provide microbial microsites and support microbial processes long-term following its application in the field. This was strongly supported by field observations (see below). Thus, nZVI use can be readily combined with biological treatment.

At the NanoRem Spolchemie II site, the application of nanogoethite particles was used as an *in situ* technology for enhancing the microbial activity with the aim to degrade BTEX contamination. The results indicated possible BTEX mass removal, but BTEX concentrations remained high.

## **3.2 Risks of deployment**

Two broad categories of risks can be foreseen during deployment: Human health risks during handling of Nanoparticles and deployment; Environmental risks towards ecology and/or groundwater from NP or / and renegade particles. These risks are either associated with the handling phase or with the deployment phase.

### **3.2.1 Human exposure and Hazards from handling**

The most significant health and safety risks for people working with nZVI are most likely to occur during the transportation, handling, and injection of the NP slurries. The most likely route of exposure to and uptake of nZVI is through dermal contact, ingestion, or inhalation. However, the likely

consequences of human exposure to nZVI are poorly understood (Moore, 2006). In vitro tests have identified that nZVI and iron oxide NPs can be toxic to a number of human and other animal cell lines, likely via the production of reactive oxygen species (Keenan et al., 2009; Blaise et al., 2008; Eun & Myung, 2007; Brunner et al., 2006). Conversely, absence of nZVI cellular toxicity is reported for some in vitro studies (Hildebrand et al., 2010). On the basis of limited testing across DNA from two species, Oberdörster et al. (2006) reported no significant toxicity issues for nZVI. Boxall et al. (2007) summarize nZVI toxicity risks with a cautionary line, while acknowledging that the environmental and human health risks are probably low.

Until recently, field-scale remediation applications of nZVI used heterogeneous slurries: either nZVI in water or in an aqueous mixture with other materials (e.g., surfactants, alcohols, etc.) More recently, air stable powder formulations have been developed and are currently commercially available. For example, Siskova et al. (2012) have demonstrated an air-stable nZVI formation coated with an inner shell of amorphous ferric oxide/hydroxide and an outer shell of glutamic acid.

Risks from handling are typically countered through pre-existing precautionary regulations which are well understood. As with health and safety regulations for other potential hazardous remedial agents (e.g., chemical oxidants), appropriate guidance for nZVI handling should follow procedures outlined in Safety Data Sheets (SDS) or, in the UK, Control of Substances Hazardous to Health (COSHH) data sheets.

### **3.2.2 Environmental risks from deployment**

Environmental risks from deployment are governed by two main factors: the travelling distance of the NPs and their eco-toxicity. The NanoRem Project produced novel information on both of these aspects.

In terms of the source-pathway-receptor paradigm used in risk-based land management (RBLM), renegade NPs are presumed to represent a hazard. Receptors in the form of not yet polluted groundwater are assumed to be present.

NanoRem laboratory and field work has helped refine our understanding of the transport of NPs. Most of the upscaling (large containers and field sites) was for porous materials. The results from the large containers and field trials showed maximum travel distances of 2.5 meters (m) and 5m respectively. NanoRem reported  $L_{T99.9\%}$  values which are predicted maximum travel distances calculated using the results of column experiments. Early experiments show predicted transport distances just over 20 m (21.8 m). Column experiments using optimized particles and a design simulating field conditions had predicted distances ( $L_{T99.9\%}$ ) of just over 30 m (32.2 m).

The Neot Hovav NanoRem site is in an industrial zone in southern Israel located over fractured chalk with high permeability fractures and a low permeability matrix. The aim of this trial was to look at transport in fractured rock. Ben Gurion University (NanoRem, 2017e) reported that the NPs travelled from the injection point to the pumping well, a distance of 47 m (Personal communication, Noam Weisbrod, [2016]). A maximum distance for NP transport in fractured rock has not been calculated, so it could exceed 47 m; further work would be required to evaluate the actual transport distances in fractured rock at this site.

Field trials and other research, which were carried out during NanoRem, has been incorporated into a risk screening model (Nathanail et al., 2016). The risk model for NP applications considers the macro-scale transport of NPs within saturated media and is based on a modified advection-dispersion

equation (Tosco et al., 2016, Bianco et al., 2015). The methodology depends on calculating values of attachment ( $k_{att}$ ) and detachment ( $k_{det}$ ) using the MNMs model (micro-and NP transport, filtration, and clogging model suite). The results of the risk screening model and the field trials and laboratory studies inform a qualitative and semi quantitative risk assessment protocol on the magnitude of risks posed by NPs that escape the zone of contaminated groundwater intended for remediation. Such renegade particles have been found not to migrate distances significant enough to pose a credible risk to unaffected groundwater, surface waters, or ecosystems.

Regarding environmental impact of reactive NPs, toxicity testing of NanoRem NPs generally found that toxicity was low; typically the limiting concentration was 100 mg/l.

These findings reinforce the view that it seems reasonable to conclude that overall risks of deployment are low.

## 4 Benchmarking and technologies cross-comparisons

Nanoremediation technology shares a number of generic benefits with other *in situ* remediation approaches such as minimizing disruption to site operations, minimizing exposure of site workers to contaminants and reagents, and reduced generation of processes waste and emissions. In common with ISBR and other forms of ISCR, nanoremediation offers the chance to avoid long-term site infrastructure required for engineered processes such as pump and treat or *in situ* air sparging.

This section makes two cross comparisons. The first is with the use of micro-scale iron for remediation and the second is with respect to the use of ISCR and ISBR.

### 4.1 Specific cross comparison with micro-scale ZVI

This sub-section is a *tentative* benchmarking of nZVI use against micro-scale iron which has been widely deployed in remediation projects, for example in permeable reactive barriers (PRBs) (Environment Agency, 2002). Indeed, comparison of the use of these two types of particles for *in situ* remediation technologies remains a challenging task as the performance of these technologies are highly dependent on *in situ* environmental conditions which are specific to each site and its subsurface characteristics. There is little literature specifically comparing the efficiency of these two-different size particles for remediation. However, in many overview or general review papers on NPs, the authors express opinions about general pros and cons on the efficiency of NPs compared with micro- or macro-scale iron. On balance, nZVI appears to offer several advantages over larger, granular-size ZVI particles as described below.

Reducing size of  $Fe^0$  materials down to nano-size **increases the surface area** by three orders of magnitude compared with granular iron, which provides a greater proportion of atoms or molecules with unsatisfied valence at the surface of the particle and a greater number of sites which are likely to adsorb or react with other atoms (e.g., Noubactep *et al.*, 2015; Hosseini *et al.*, 2015; Guan *et al.*, 2015; Tosco *et al.*, 2014; Yirsaw, 2016).

**Degradation kinetics** are usually considered to be significantly faster for NPs than micro-scale particles. Based on reaction rate (KM - mass normalized pseudo first order reaction rate), nZVI can degrade contaminants one or two orders of magnitude faster than micro-scale ZVI (Velimirovic, 2013). However, based on KSA (surface area normalized reaction rate constant), the reactivity of newly produced micro-scale ZVI was similar to the highly reactive nZVI and even higher (Velimirovic, 2013).

This tends to show that the reactivity of the nZVI is very much linked with the increased surface area of nZVI. The higher reactivity of nZVI allows to degradation of some contaminants (for example PCBs) which are hardly degraded by mmZVI or  $\mu\text{mZVI}$ .

NPs are **able to migrate** farther in soil and groundwater compared with micro-scale ZVI which is essentially immobile (Mueller, 2012; Lefèvre, 2016).

NPs are thought to be promising **remediation for source zones**, which in some cases is believed to be faster and more effective compared to other groundwater treatment technologies such as pump and treat or PRBs (Comba, 2011; Tosco, 2014; Yirsaw, 2016). In addition, it appears likely that nZVI has a better performance regarding the range of treatable contaminants, the extent and the speed of contaminant destruction, and the range of environmental conditions which can be tolerated, as noted in Section 3.2. Microscale iron also stimulates *in situ* biodegradation (see Section 3.5), but potentially nZVI may have a more dramatic effect on changing redox potential and microbial hydrogen availability.

However, some drawbacks of iron NPs have also been highlighted when compared to their bigger counterparts and are described below.

**Aggregation, agglomeration and corrosion** (and associated volumetric corrosion products) are passivation mechanisms which are predominant for nZVI and affect their reactivity (Noubaptec, 2012; Hosseini, 2015). According to Velimovic experiments (2014), micro-scale ZVI has approximately a 10 to 30 times lower corrosion ratio than nZVI. As less reactive particles will sustain reducing conditions for longer times and provide better performance, micro-scale ZVI is known to have **a longer longevity** than nZVI (Comba, 2011). **The lower persistence of nZVI** is due to its higher reactivity. Hence, unsurprisingly, persistence of  $\text{Fe}^0$  in the subsurface decreases with the size of the Fe particle (millimeter ZVI having longer persistence than micron-ZVI than nZVI (Noubaptec, 2012). Hence there is a balance to be struck between the treatment effectiveness, which is higher for nZVI, versus its likely persistence in the subsurface which is likely to be lower compared with larger  $\text{Fe}^0$  particles.

#### 4.2 Cross comparison with principal remediation alternatives

To date, land contamination problems addressed by nanoremediation relate to source control and/or pathway management for NAPLs, such as chlorinated solvents, and hazardous elements such as arsenic or chromium (see Section 3.11). These relatively few contaminants are highly prevalent problems, according to a 2014 report by the European Commission's Joint Research Centre in ISPRA, and account for perhaps more than 50% of contamination problems in Europe (JRC, 2014).

The main competing *in situ* remediation alternatives to nanoremediation for non-aqueous phase liquids (NAPLs), such as chlorinated solvents, and hazardous elements such as dissolved As or Cr(VI) species are ISBR and conventional forms of ISCR using reducing agents (Nathanail, *et al.*, 2007) such as micro-ZVI sodium dithionite or calcium polysulphide (US EPA 2018).

As stressed in the synergy section above, use of nZVI can also be stimulatory for ISBR, and support completion past known potential stall points for ISBR (Kocur *et al.*, 2015). Similar synergies are exploited in commercial reagents for ISCR using microscale ZVI (Peroxychem 2018), but NPs are more rapidly effective.

Conventionally, ISCR and ISBR are primarily pathway (plume) management intervention with limited scope to address source areas; they have limited effectiveness against several important contamina-

tion issues such as fuel oxygenates, fluoridated organics, and various other recalcitrant contaminants. In addition, ISCR and ISBR may be modify aquifer properties that render them unacceptable in some circumstances; and ISBR may be subject to process stall.

The NanoRem project has developed a range of supporting deployment risk assessment and sustainability assessment tools (available from [www.nanorem.eu/toolbox/index.aspx#TB1](http://www.nanorem.eu/toolbox/index.aspx#TB1)) to ensure that nanoremediation is safe, effective and sustainable, with a level of scrutiny that far exceeds that which has been required for many of the subsurface amendments required to initiate ISBR or ISCO/R.

**Error! Reference source not found.** provides a comparative benchmarking across risks and benefits for nanoremediation and its two main competitor approaches ISBR and ISCR. Cost indications in **Error! Reference source not found.** are based on a Czech case study (Kvapil *et al.*, 2016). **Error! Reference source not found.** provides a more complete comparison of the relative costs used for nanoremediation to bioremediation (using lactate injection) and ISCR using microscale ZVI alone. The comparison is based on a Czech example and a Czech cost base. It is only illustrative, and there are generally few hard and fast rules for cost estimation for *in situ* remediation technologies. The modelled application is for a pathway management of a chlorinated solvent plume, and is benchmarked against nanoremediation in percentage terms. It is based on treatment to Czech regulatory thresholds within three years. In this example, ISBR is substantially cheaper than nanoremediation.

**Exhibit 1** Benchmarking costs, risks, and benefits of nanoremediation compared to ISBR and ISCR

		Nanoremediation	Conventional ISCR	ISBR
<b>Risks</b>	<b>Human health</b>	Some NPs are hazardous, some are air stable and safer to handle. No exposure once successfully deployed.	Some reagents, such as dithionate, are potentially hazardous. No exposure once successfully deployed.	Materials are safe to handle. No exposure once successfully deployed.
	<b>Aquifer ecology</b>	Injections are typically in highly disturbed environments. No NP specific ecotoxicity found by NanoRem. Ultimate fate is as iron oxides which are plentiful in soils.	Injections are typically in highly disturbed environments. Ecological impacts unstudied, but assumed minimal.	Injections are typically in highly disturbed environments. Ecological impacts unstudied, but in the long terms assumed minimal <sup>1</sup> .
	<b>Water</b>	Injected materials have limited lifetimes and limited travel distance, and are not associated with adverse effects of subsurface groundwater quality.	Lifetimes and travel distance of injected dithionite has not been widely studied, may be extensive. The travel distance of mZVI is essentially zero. High levels of sulfate and low pH remaining after dithionate or polysulfide reduction	Injected substrates to stimulate bioremediation are soluble or release soluble substrates possibly adversely affecting groundwater quality <sup>2</sup> .
	<b>Supporting measures</b>	Pre-deployment risk assessment available and published.	No pre-deployment risk assessment tool.	No pre-deployment risk assessment tool.

<sup>1</sup> Note ISBR is mediated by deliberate modification of aquifer ecology to stimulate dehalorespiration.

<sup>2</sup> This concern has led regulators in some regions to prevent ISBR deployment in some cases, e.g. at the Písečná site, CZ

		<b>Nanoremediation</b>	<b>Conventional ISCR</b>	<b>ISBR</b>
<b>Benefits</b>	<b>Breadth of solutions</b>	Wide range of treatable contaminants. Source area and pathway management applications. Suitable for situations inhibitory to microbial dehalorespiration processes.	Wide range of treatable contaminants. Tendency to pathway management applications. Suitable for situations inhibitory to microbial dehalorespiration processes	More restricted range of treatable contaminants. Potential for stall (e.g. TCE --> DCE) Tendency to pathway management applications. May be prevented by toxic or other inhibitory conditions
	<b>Speed and completeness of action and synergies</b>	Rapid treatment effects owing to nanoscale processes. Moderate migration in the subsurface. Tendency to complete degradation of contaminants. Synergistic with ISBR and ISCR.	Slower treatment effects. Microscale ZVI does not readily move in the subsurface. Tendency to complete degradation of contaminants. Synergistic with ISBR and nanoremediation	Slower treatment effects. Soluble substrates migrate rapidly in the subsurface Tendency to stall for some problems <sup>3</sup> . Synergistic with nanoremediation and ISCR.
	<b>Ease of deployment</b>	Portable systems (not requiring fixed infrastructure). Some systems require specialized deployment interventions. NanoRem is addressing the issue that deployment knowledge is limited <sup>4</sup> .	Portable systems (not requiring fixed infrastructure). Widespread knowledge and systems.	Portable systems (not requiring fixed infrastructure). Widespread knowledge and systems.
	<b>Track record</b>	Limited track record, relatively few suppliers.	Well established technology, many vendors, moderate track record.	Well established technology, many vendors, substantial track record.
<b>Costs</b>	<b>Cost estimating</b>	Bespoke cost estimates required for each deployment option appraisal.	Many consultants have a good knowledge of relative treatment costs.	Many consultants have a good knowledge of relative treatment costs.
	<b>Relative Cost levels</b>	100%	70-90%	60%

<sup>3</sup> E.g., stall at DCE, which may then require additional intervention such as bioaugmentation with *Dehalococcoides*.

<sup>4</sup> Inappropriate deployment can be associated with failure to reach target volumes and even daylighting to the surface

**Exhibit 2** Cost benchmarking of remediation options for an example contaminant plume (Kvapil *et al.*, 2016)

	nZVI	ISCR (micro)	ISBR
Material mass (bulk) [%]	100%	500%	1000%
Material costs [%]	100%	20%	10%
No of injections / total time	6 injections / 2 years	6 injections / 3 years	9 injections / 3 years
Operation costs [%]	100%	250%	150%
Monitoring costs [%]	100%	150%	150%
<b>Total costs [%]</b>	<b>100%</b>	<b>90%</b>	<b>60%</b>
Risk of failure	100%	130%	70%

## 5 Concluding remarks

Nanoremediation may offer notable advantages in some remediation applications. These benefits are site specific and niche rather than representing some kind of over-arching step change in remediation capabilities. The principal constraints remain perceived cost and availability of cost and performance data from “real” applications, as opposed to pilot deployments in the field and, in some cases, regulatory reluctance at a local level in some regions. Nonetheless, NanoRem has achieved a major shift in the technical discussion of nanoremediation across many practitioners in the international contaminated land management market, in that it is now seen as a viable option, albeit it at the “early adoption” stage, rather than being seen as an emerging approach of fringe interest. There has always been a minority interest in the technology, but NanoRem has succeeded in placing it as something worthy of consideration by many more service providers.

The perception of risk-benefit balance has also shifted. Niche benefits are now more strongly recognized, and some (if not most) of the concerns, for example relating to environmental risks of nanoremediation deployment, prevalent when the NanoRem project was proposed and initiated, have been addressed. These now appear overstated. However, it appears to remain the case that in some jurisdictions (e.g., the UK) the use of NPs remains less attractive owing to regulatory concerns, and in others (e.g., in Italy) impeded by a lack of awareness, meaning that regulators may demand additional verification measures compared with technologies with which they have a greater level of comfort. In both cases a higher level of regulatory scrutiny imposes additional project costs and complexities which make nanoremediation less appealing as a practical and cost effective remediation option. Acceptability depends critically on the availability of well documented case studies (Bartke *et al.*, 2018)

The underpinning constraint does seem to be perceived cost, as reduction in perceived cost would likely encourage greater interest in field scale testing and, hence, a more robust track record of deployment experience. One possible route to cost reduction is combining nano and micro-scale ZVI use. One example of this is the development by some the Czech NanoRem partners of a combined nano/micro ZVI technology that also exploits electrochemical processes to maintain nanoscale activity that exploits their differences in persistence and behaviour to produce a more robust treatment solution (Miroslav Černík, Technical University of Liberec, Personal Communication).

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## AUTHOR BIOGRAPHIES

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tion of Groundwater Resources at Industrially Contaminated Sites) and coordinator of NanoRem from 2013 to 2017.

## 7 Supplemental Materials

### Overview Table of NP Field Applications Identified Worldwide, as of November 15, 2016

Extended and adapted from Bardos *et al.*, 2011

Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Con- centration	Injection Technique (Technology De- sign)	NP Type	Amount Applied
Belgium Herk-de-Stad, CITYCHLOR Consortium. 2013	Pilot	Mixed permeability aquifer	GW	Chlorinated solvents (PCE and daughters)	Some free product suspected	Direct Push Injection	nZVI	
Canada, Brownfield, SK, Müller and Nowack 2010	Pilot	Unconsolidated sediments	Soil	TCE, DCE				
Canada, London, Ontario, Chowdhury <i>et al.</i> , 2015	Field test	Sandy silt aquifer	GW,	TCE		nZVI was injected into an existing well	nZVI produced on site	0.14 kg
Canada, Sarnia Site, Ontario, Karn <i>et al.</i> , 2009 <i>Supplemental Material</i> (O'Carroll 2014), Kocur <i>et al.</i> , 2014 and 2015	Pilot	Unconsolidated sediments	GW	PCE, TCE	TCE 86,000 µg/L	Gravity injection at four points	nZVI synthesised on site, stabilised with CMC	700 L of 1 g/L nZVI with 0.8 wt % CMC polymer
Canada, Valcartier Garrison Quebec***, US EPA 2016 <sup>5</sup>	Pilot	Alluvial sands and gravel, glacial sands, silts and gravels (deltaic and proglacial sands)	GW, Sands and clayey silts	TCE, DCE, VC	TCE: ~300 µg/L; DCE: ~50 µg/L	Injection Screen Wells	nZVI with a palladium catalyst with a soy powder surface modification	4.5 tonnes (A future full scale application is envisaged of 100 tonnes)
Czech Republic, Spolchemie, Usti nad Labem, Site 1*,	Pilot	Quaternary sand and gravel underlain by a clay	GW	DNAPLs (chlorinated solvents)		Direct push	nZVI, <i>NANOFER</i> 25s and <i>NANOFER</i>	Injection 1: 200kg <i>NANOFER</i>

<sup>5</sup> As of 2012 Golder's have deployed on 20 field sites in total (Lilley 2012). Lilley, F. (2012). Golder's Project Experience with Nano Scale Zero Valent Iron Retrieved from [http://s3.amazonaws.com/ebcnc-web-content/fileadmin/pres/4-10-2012\\_Nanoremediation/4-10-2012\\_Lilley.pdf](http://s3.amazonaws.com/ebcnc-web-content/fileadmin/pres/4-10-2012_Nanoremediation/4-10-2012_Lilley.pdf).

Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	NP Type	Amount Applied
(NanoRem Consortium 2017)		aquitard					STAR (air stable)	25s; Injection 2 ~600 kg NANOFER STAR
Czech Republic, Spolchemie, Usti nad Labem, Site 2*, NanoRem Consortium 2017	Pilot	Quaternary sand and gravel underlain by a clay aquitard	GW	LNAPL (BTEX, primarily toluene),		Direct push	Nano-goethite (nano-iron oxide) - used to stimulate microbial activity	Test 1 60 kg Test 2 300 kg
Czech Republic, Hluk**, Müller and Nowack 2010	Pilot	PRB filter	GW	Chlorinated Ethenes	5 mg/l	Infiltration Wells	RNIP <sup>6</sup> , Nanofer <sup>7</sup>	300 kg
Czech Republic, Horice**, Müller and Nowack 2010, Müller <i>et al.</i> , 2012	Full	Low permeable aquifer	GW	PCE (TCE, DCE)	70mg/l	High pressure pneumatic injection	nZVI (RNIP and Nanofer)	2 tonne
Czech Republic, Kurivody**, Müller and Nowack 2010	Several Pilot/Full	Fractured bedrock	GW, overburden, weathered bedrock	Chlorinated Ethenes	15 mg/l	Infiltration wells, infiltration drains	nZVI, RNIP, Nanofer**	100s kg
Czech Republic, Permon**, Müller and Nowack 2010	Pilot	Fractured bedrock	GW	Cr(VI)	450 mg/l	Infiltration wells	nZVI, RNIP	150 kg
Czech Republic, Piestany**, Müller and Nowack 2010	Pilot	High permeable aquifer	GW	Chlorinated Ethenes	5 mg/l	Infiltration wells	nZVI synthesised on site	20 kg
Czech Republic, Pisečna**, Müller and Nowack 2010, Müller <i>et al.</i> , 2012	Full	Sandy / silt	GW	Chlorinated Ethenes chlorinated Ethanes	35 mg/l	High pressure pneumatic injection	nZVI, RNIP, Nanofer	4.5 tonnes of RNIP and Nanofer
Czech Republic, Rozmital**, Müller and Nowack 2010	Full	Fractured bedrock	GW	PCB	2 mg/l	Infiltration wells	nZVI, RNIP, Nanofer	1 tonne

<sup>6</sup> RNIP were the nZVI nanoparticles produced by Toda Corporation in Japan (these are no longer in production)

<sup>7</sup> The producers of Nanofer state that they have additional deployments in the Czech Republic and also pilot deployments in Italy, Spain, France, Belgium, Netherlands, Canada, South Korea, and Hungary: usually 50-300kg of nZVI. However, they are not permitted to disclose further information. ###

Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	NP Type	Amount Applied
Czech Republic, Spolchemie**, Müller and Nowack 2010	Several Pilot/Full	Porous aquifer	GW	Chlorinated Ethenes, chlorinated Methanes	40 mg/l	Infiltration wells	nZVI, <i>Nanofer**</i>	Several tonnes
Czech Republic, Uhersky Brod**, Müller and Nowack 2010	Pilot	Porous aquifer	GW	Chlorinated Ethenes		Infiltration wells	nZVI, <i>Nanofer</i>	150 kg
Czech Republic, Uzin**, Müller and Nowack 2010	Pilot	Low permeable aquifer	GW	Chlorinated Ethenes	20 mg/l	Infiltration drains	nZVI, <i>Nanofer</i>	300 kg
Denmark, Taastrup; Danish Environmental Protection Agency-2015	Pilot	Low permeable glacial clay moraine deposits	unknown	unknown	unknown	High pressure injection	nZVI	unknown
Denmark, electrical substations at three locations, Danish Environmental Protection Agency-2015, Hindrichsen <i>et al.</i> , 2015	Pilot	The overall geology for the three sites, is clay till with various contents of sand lenses underlain by a sandy secondary aquifer	GW (sandy aquifer)	PCE and TCE)and their degradation products DCE and VC		Injection, in one location pre-injection with molasses	nZVI (NANOFER 25S)	Site 195 kg; site 2, 200 kg; site 3 several tonnes in two campaigns
France, PRODEM site, Toulouse**	Pilot	Low permeable aquifer	GW	Chlorinated Ethenes, Cr(VI)	7 mg/l	Infiltration well	nZVI, <i>Nanofer</i>	150 kg
France, SNG site near Chalon sur Saone**	Pilot	Porous aquifer	GW	Chlorinated Ethenes, CN	30 mg/l, 20 µg/L	Infiltration well	nZVI, <i>Nanofer</i>	25 kg
Germany, Asperg, Müller and Nowack 2010	Pilot	Fractured rock	GW	Chlorinated Ethenes		Sleeve-pipe injection	nZVI, RNIP	
Germany, Bornheim, Müller and Nowack 2010, Müller <i>et al.</i> , 2012	Full (first European full scale application)	Sandy gravel		PCB, TCB, PCE, TCA, Pesticide, solvents, perchlorates		Sleeve-pipe injection	nZVI, RNIP**	1 tonne nZVI and two tonnes micro ZVI
Germany, Gaggenau, Müller and Nowack 2010	Pilot	Porous aquifer	GW	PCE		Sleeve-pipe injection	nZVI, RNIP	
Germany, Hannover, Müller and Nowack 2010	Pilot	Chemicals storage facility	Soil and GW	CHC, BTEX. HC		Aqueous slurry	Not specified	
Germany, Schönebeck Müller and Nowack 2010	Pilot	Porous aquifer	GW	VC		Push infiltration	nZVI, RNIP	
Germany, site Breite St. in Braunschweig, Kober	Pilot	Porous aquifer	GW	PCE	20 to 50mg/L	Direct push injection	Milled ZVI with a flake-like	280 kg

Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Con- centration	Injection Technique (Technology De- sign)	NP Type	Amount Applied
<i>et al.</i> , 2014							shape and thickness of <100 nm	
Germany, Thuringia, Müller and Nowack 2010	Pilot	Porous aquifer	GW	Chlorinated aliphatic hydrocarbons, Ni, Cr, NO <sub>3</sub>	CAH: 104,000 µg/L Ni: 4,130 µg/L Cr: 1,460 µg/L NO <sub>3</sub> : 70 mg/L	Injection wells	nZVI	120 kg
Hungary, Balassagyarmat*, NanoRem Consortium 2017	Pilot (plume test no access to source)	Made ground (fill) over alluvial deposits over a bedrock aquitard	GW	Chlorinated hydrocarbons, PCE, TCE, DCE		Direct injection	Carbo-Iron® stabilised in CMC (nZVI sorbed to activated carbon)	177 kg
Hungary (industrial site, confidential), 2014 *****	Full	Unconsolidated sediments	GW	cDCE, VC		Direct injection	nZVI	5,300 kg
Hungary (industrial production site, confidential), 2015 *****	Full	Unconsolidated sediments	GW	TCE		Direct injection	nZVI	500 kg
Hungary (chemical storage facility, confidential), 2014 *****	Extended Pilot	Mixed sands	GW	Contaminant mix, volatile aromatic chlorinated hydrocarbons treated		Reactive barrier and direct injection	nZVI	700 kg
Israel Neot Hovav*, NanoRem Consortium 2017	Pilot	Fractured bedrock (Eocene chalk)	High salinity GW	Not specified		Not specified	Carbo-Iron® stabilised in CMC (nZVI sorbed to activated carbon)	Not specified
Israel, Nir Galim, Jacov <i>et al.</i> , 2012	Pilot		GW	PCE, TCE, dis-DCE		Groundwater directed through column containing nZVI composite	Diatomite supported nZVI-vitamin B12 composite.	50kg
Italy, Biella, Müller and Nowack 2010	Pilot	Porous aquifer	GW	TCE, DCE		Gravity infiltration	nZVI	
Netherlands, Rotterdam, Citychlor Consortium 2013	Full	Not specified	GW	Chlorinated solvents (PCE and daughters)		Injection	nZVI	Not specified
Portugal, Lousal, #	Pilot	Low permeable aquifer	GW	Heavy metals		Injection wells	Nanofer 25S	500kg

Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Con- centration	Injection Technique (Technology De- sign)	NP Type	Amount Applied
Portugal, Lisbon ****	Pilot	Porous aquifer below made ground	GW	Heavy metals, (As, Pb, Zn, Cd, Cu and Ni)		Gravity injection	Nano-goethite (nano-iron oxide)	300 kg
Spain, Nitrastur*, NanoRem Consortium 2017	Pilot	Made ground (2 to 9 m deep)	GW	Petroleum hydrocarbons and heavy metals (As, Pb, Zn, Cd, Cu and Ni)	Highest level of dissolved As found 5527 µg/l	Gravity feed to wells	nZVI, NANOFER STAR	250 kg
Spain, Nitrastur, Asturias Region ****	Pilot	Porous aquifer below made ground	GW	Heavy metals, (As, Pb, Zn, Cd, Cu and Ni)		Gravity injection	Nano-goethite (nano-iron oxide)	300 kg
Switzerland, industrial site*, NanoRem Consortium 2017	Pilot	Primary source is constrained by a barrier wall and secondary by a P&T, highly permeable alluvial aquifer (sand+gravel) over bedrock (weathered or not opalinus clay)	Soil (weathered marlstone – secondary source) and GW	DNAPL, primarily PCE, Hexachloroethane, TCE and Hexachlorobutadiene	Maximum overall levels ~20,000 mg/kg	Injection under pressure into dedicated wells	First injection: Milled iron, second: nZVI + micro-iron	500 kg + 300 kg nZVI mixed with 200 kg of micro-iron
Taiwan, Kaohsiung; Karn <i>et al.</i> , 2009 <i>Supplemental Material</i> , Wei <i>et al.</i> , 2010	Pilot	Medium - coarse sand unconfined aquifer, 4-18m bgs	Unconfined aquifer	TCA, TCE, DCA, DCE, Vinyl chloride	VC 620-4,562 µg/L, EDA 207 µg/L, DCE 1,151 µg/L, TCE 682 µg/L	Gravity feed injection	nZVI, Pd-nZVI, commercial and synthesised	40kg nZVI in 2250L dilution (commercial); 20kg in 8500L dilution (synthesised).
USA, Aberdeen, MD, Karn <i>et al.</i> , 2009 <i>Supplemental Material</i>		Not specified		1,1,2,2-TeCA, 1,1,1-TCA, TCE, Cr(VI)			nZVI	
USA, Active Business Site Dayton, Ohio, US EPA 2016	Pilot	Not specified	GW	PCE, TCE	TCE: 50 µg/L ; PCE:150 µg/L	“Injections”	Iron-Osorb™. nZVI-silica hybrid NPs	45 kg
USA, Aerospace facility, San Francisco Bay, CA, Bennett <i>et al.</i> , 2010, Krol <i>et al.</i> , 2013	Full	Course alluvial silt clay sediments	GW	PCE, TCE		Multi-level push-pull	CMC stabilised nZVI and BNP - nZVI-Pd	~140 g NZVI ~ 120 g BNP

Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Con- centration	Injection Technique (Technology De- sign)	NP Type	Amount Applied
USA, Alameda Point, CA, US EPA 2016	Pilot	Not specified	GW	TCE	Average 2,500 µg/L	Direct injection	Surface modi- fied nZVI	500 gallons slurry (con- centration of nZVI not specified)
USA, Camp Pendleton Southern California; ES EPA 2016	Pilot (possi- bly bench scale)	Not specified	GW	TCE		<i>Ex situ</i> treatment	nanoscale zero valent zinc	
USA, Cape Canaveral Launch Complex 15, FL, US EPA 2016	Full	Groundwater; surficial aquifer; fine/ medium sandy silts	Soil and GW	TCE	439,000 µg/L Max TCE found	Drop tip injection	Emulsified nZVI (EZVI)	Described as a <i>full scale</i> project
USA, Cape Canaveral, Launch Complex 34, FL, US EPA 2004; US EPA 2016	Pilot	Surficial aquifer with fine / medi- um grained sands	Soil and GW	TCE	1,180,000 µg/L Max TCE found	High pressure pneumatic injection and pressure pulse enhanced injection	Emulsified nZVI (EZVI)	670 US gal- lons of EZVI (17% iron by mass)
USA, Edison, New Jersey, US EPA 2016	Pilot and Full	Fractured bruns- wick shale bed- rock and 4-6ft of silt and clay soil	Fractured Bed- rock	TCA, TCE, DCA, DCE, cholorethane, vinyl chloride	TCA 13,000 to 1,200,000 ppb)	Injection wells	nZVI and emul- sified vegetable oil (nZVI con- tent not speci- fied)	10,000 US gallons
USA, Former Manufac- turing Site Bridgeport, Ohio, US EPA 2016	Pilot (possi- bly only bench scale)	Not applicable	GW	TCE, DCE, VC	Total to 5,800 µg/L	<i>Ex situ</i> treatment		
USA, Frankling Square, New York, Karn <i>et al.</i> , 2009 <i>Supplemental Ma- terial</i>				PCE, TCE, 1,1,1-TCA, Cr(VI)			nZVI	
USA, Hamilton Landfill, New Jersey, Karn <i>et al.</i> , 2009 <i>Supplemental Ma- terial</i>				1,1,-TCA, 1,1-DCA, 1,1- DCE, Pb, Ni			nZVI	
USA, Hamilton Township Trenton , New Jersey, US EPA 2016, Elliott and Zhang, ES&T (2001),	Proof of concept (2000) and field pilot3	Middle potomac raritan magothy (mprm) aquifer. Shallow uncon-	GW	TCE, DCE, CT	400 - 3000 µg/L	2000: injection well delivery (2 phases) with recirculation 2003: direct push	2000 Proof of concept – nZVI/Pd synthe- sized by Lehigh	2000: approx. 1.7 kg 2003: approx. 25 kg

Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Con- centration	Injection Technique (Technology De- sign)	NP Type	Amount Applied
Zhang et al (2006)	(2003, 2007)	finned sandy aquifer (approx. 7 feet bgs to approx. 25 feet bgs).				injection 2007: direct push injection	University 2003 Pilot – nZVI from PARS 2007 Pilot – nZVI from Lehigh Nano- tech LLC	2007: approx. 220 kg
USA, Hampton, SC, Karn <i>et al.</i> , 2009 <i>Supplemental Material</i>		Silty to fine sand from 25 - 45 feet bgs - then dense clay	GW	TCE, PCE	TCE 300 ppm		nZVI	
USA, Hanford Site Department of Energy, Washington State, US DOE 2009	Pilot	Sandy gravel to silty sandy gravel 3 to 9 m thick. Retrofit to an existing well based sodium dithionite prb	GW	Dissolved Cr (VI)	Circa 1000 µg/L	Injection into existing well under slight pressure (1.8 m head of water).	nZVI (Toda RNIP-M2)	3710 kg
USA, Hill Air Force Base Operable Unit 2, Utah; US EPA 2016		Coarse-grained soils and overlying clay, silt, and fine sand	Soil and groundwater	TCE	TCE: 12 mg/kg (Max in soil); TCE: 14.3 mg/L (Max in groundwater)	Well “injection”	Stabilized Fe-Pd bimetallic NPs with CM.	5.2 kg
USA, Industrial site, Ironton, Ohio, US EPA 2016	Pilot	“Complex hydrogeology”	GW	TCE	TCE: 60 to 250 µg/L	“Injection”, preferential flow along “seams” reported	Iron-Osorb™. nZVI-silica hybrid NPs	
USA, Jacksonville, Florida, FRTR 2006; Gavaskar <i>et al.</i> , 2005; US EPA 2016	Full	Silt / fine sands(0-24ft) and dense clay (24-54ft). Source zone treatment	Soil and GW	TCE, TCA, DCE, vinyl chloride	Max soil concentrations: PCE: 4,360 µg/kg; TCE: 60,100 µg/kg; 1,1,1-TCA: 25,300 µg/kg. Max GW concentrations PCE: 210 µg/L; TCE: 26,000 µg/L; 1,1,1-TCA: 8,400 µg/L; cis-1,2-DCE: 6,700 µg/L	Direct push / closed loop recirculation	BNP	135 kg
USA, Kearny, New Jersey,				Cr(VI)			nZVI	

Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Con- centration	Injection Technique (Technology De- sign)	NP Type	Amount Applied
Karn <i>et al.</i> , 2009 <i>Supplemental Material</i>								
USA, Lakehurst, New Jersey, FRTR 2006; Gavaskar <i>et al.</i> , 2005; US EPA 2016	Full	Two plumes tested: sand / gravel coastal plain aquifer	Soil and GW	PCE, TCE, TCA, c-DCE, vinyl chloride	900 µg/L	Direct push	BNP	1360 kg (2005) and 225 kg (2006)
USA, Manufacturing Plant Middlesex County, New Jersey; US EPA 2016	Pilot	Made ground (fill) underlain by a moderately fractured shale bed-rock	Soil and groundwater	TCE and daughter compounds	~500 µg/L	Two separate "injection events"	nZVI	410 kg
USA, Mechanicsburg, PA, Karn <i>et al.</i> , 2009 <i>Supplemental Material</i>		Fractured rock	GW	TCE			nZVI with Pd	
USA, Newfields, New Jersey, Karn <i>et al.</i> , 2009 <i>Supplemental Material</i>				TCE, cis-DCE, Cr(VI)			nZVI	
USA, North Slope, Prudhoe Bay, Alaska (abandoned oil field) AK, US EPA 2016	Pilot	Organics over alluvial gravels	Soil	TCA, diesel fuel	Max TCA level 58,444 ug/Kg	Tested shallow physical mixing and pressurised injection at depth	BNP	
USA, Northern Alabama, (abandoned metal processing plant ), US EPA 2016, Zhao and He 2007	Pilot	Heterogeneous relatively shallow semi-confined aquifer.	Soil and GW	PCE, TCE and PCB's	TCE MW-1 (1655 µg/L) MW-2 (2710 µg/L)	Gravity feed injection	CMC stabilised BNP	150 US gallons of 0.2 g/L Fe-Pd NP suspension
USA, Palo Alto, CA, US EPA 2016	Pilot	<i>Ex situ</i> testwork	GW	PCE, TCE, Freon	PCE (26,000 µg/L); TCE (70,000 µg/L);	<i>Ex situ</i> , field batch reactor	Starch-stabilized BNP (Fe/Pd)	
USA, Parris Island, Marine Corps Depot former dry cleaners, South Carolina, Krug <i>et al.</i> , 2010; Su <i>et al.</i> , 2012 & 2013; US EPA 2016	Pilot	Shallow unconfined aquifer permeable, fine to medium sand to a depth of 5.2mbg	Soil and GW	PCE, TCE, c-DCE, vinyl chloride	PCE (32,000 µg/L); TCE (10,000 µg/L); c-DCE (3,400 µg/L); Vinyl Chloride (710 µg/L) Max levels found	Direct push and pneumatic injection	Emulsified ZVI (EZVI) Emulsified on site using nZVI	0.25 m3 EZVI over both injection plots (consisting of 10% nZVI, 38% corn oil, 1% surfactant and 51% tap water.

Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	NP Type	Amount Applied
USA, Passaic, New Jersey Manufacturing Site, US EPA 2016, Zhang <i>et al.</i> , 2006	Pilot	High permeability sands (to 21 ft bgs) with silt lens (21-26 feet bgs)	Soil and GW	TCE	Total VOC concentrations range 450 to 1,400 µg/L. Most of the contaminant mass was bound in a low permeability silt unit.	The nZVI and emulsified oil were emplaced using three injection points directly into the silt lens. Pneumatic fracturing injections were used at two points and hydraulic injection at the other	nZVI and emulsified vegetable oil. ZVI combined with biostim	49 kg of nZVI slurry of unknown nZVI concentration and 55 kg of emulsified oil
USA, Patrick AFB, FL, US EPA 2016	Full	Groundwater; surficial aquifer; fine/ medium sandy silts	Soil and GW	TCE (and daughter contaminants)	150,000 µg/L (max level TCE found)	High pressure pneumatic injection	Emulsified ZVI (EZVI)	N/A
USA, Penn-Michigan, West Lafayette, Ohio, US EPA 2010; US EPA 2016	Pilot (three locations)	Sand and gravel aquifer with a high groundwater flow	GW	TCE	250 - 1,000 µg/L	Direct injection	nZVI-silica hybrid NPs (at one location with palladium) ( <i>Iron-Osorb<sup>TM</sup></i> )	94 kg material in total
USA, Pharmaceutical Facility, Research Triangle Park, NC, US EPA 2016	Pilot	Triassic basin sandstone interbedded with siltstone grading downwards into mudstones	GW in fracture bedrock	PCE, TCE, DCE, VC	The max concentration of VOCs was around 14,000 µg/L.	Injection wells	BNP	1.9 µg/L of BNP slurry The total NP mass injected was 11.2 kg.
USA, Goodyear, AZ, (Phase I) , US EPA 2016	Pilot	Alluvial deposits of western salt river valley. Impacted groundwater zone from 85-150 feet bgs. Consisting of upper alluvial unit, middle fine grained unit, lower conglomer-	GW	TCE, PCE, perchlorate	Up to 39,000 µg/L total VOCs. Perchlorate up to 150 ppb.	The field injection test consisted of the injection of 30 g/l nZVI slurry in water through one injection well. Note the formation was "clogged" by injection.	nZVI	Approx. 10 kg

Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Con- centration	Injection Technique (Technology De- sign)	NP Type	Amount Applied
		ate unit and groundwater at 85 ft						
USA, Phoenix, Goodyear, AZ, (Phase II), US EPA 2009a, US EPA 2016	Pilot	As above	GW	TCE, PCE, perchlorate	Total contaminant concentration ranged from 3,500 to 11,000 µg/L	Injection wells	nZVI	10,400 litres of a 2.1 g/L nZVI slurry (total of 22 kg)
USA, Phoenix, Goodyear, AZ, (Phase III), Haley & Aldrich, Inc. 2011, US EPA 2016,	Pilot	As above	GW	TCE, PCE, perchlorate	Max baseline concentrations detected (µg/L): PCE: 3 TCE: 6,300 cis-1,2-DCE: 2	“Jet lance injection tool”	Stabilised nZVI (~90% nZVI; 5% polyacrylate, 5% SHMP <sup>8</sup> , 0.5% guar gum by mass)	~640 kg
USA, Picatinny Arsenal Superfund Site, New Jersey, US EPA 2009b; US EPA 2016	Pilot	“Organic rich soil”	GW	CCl <sub>4</sub> , TCE	CCl <sub>4</sub> : 250 µg/L; TCE: 87 µg/L	Injection via temporary wells	nZVI ( <i>Ferragel</i> )	~54 kg
USA, Ringwood, New Jersey, US EPA 2016	Full	N/a	GW	TCE, Bis(2-Ethylhexyl)phthalate, Benzo[a]Anthracene	TCE (1.1 µg/L); Bis (2-Ethylhexyl) phthalate (9.8 µg/L); Benzo[a]Anthracene (0.14 µg/L)	Push injection	Nano - Ox™	375 kg
USA, Rochester, NY (aircraft testing facility)***	Pilot	Aquifer consisting of mostly sand and gravel, two plumes tested	Soil and GW	PCE, TCE, TCA, DCE, Vinyl Chloride	Maximum VOC concentration: 900 µg/L	Direct push	BNP	1.4 tonnes total
USA, Rochester, NY, (former manufacturing plant)***	Pilot	Glacial till overburden lying above fractured sedimentary bedrock	GW in till and bedrock	TCE	Circa 1,000 µg/L	Direct push ( <i>geoprobe</i> )	nZVI	10-20g/L nZVI slurry (total mass nZVI 60 kg)

<sup>8</sup> Sodium hexametaphosphate

Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Con- centration	Injection Technique (Technology De- sign)	NP Type	Amount Applied
USA, Rochester, NY, (former manufacturing plant), US EPA 2016	Pilot	Glacial till over- burden overlying fractured sedi- mentary bedrock	GW in bedrock	Methylene chloride, 1,2-dichloropropane, 1,2-dichlorethene	Total contaminant concentration: 500,000 µg/L	Gravity feed injec- tion	nZVI	10-20g/L nZVI slurry (total mass nZVI 100 kg)
USA, Rock Hill, SC, Karn <i>et al.</i> , 2009 <i>Supplemental Material</i>		Unconsolidated sediments	GW	TCE, DCE			nZVI	
USA, Rockaway Town- ship, New Jersey, US EPA 2016	Pilot	Organics rich soil	GW	Carbon tetrachloride, TCE	CCL4 (250 ppb); TCE (87 ppb)	Injection wells	nZVI	54 kg of nZVI over 2 wells
USA, Salem, OH, US EPA 2007; US EPA 2016	Pilot	Glacial till over fractures sedi- mentary bedrock	GW in fracture bedrock	PCE, TCE, DCE, VC	PCE: 80 mg/L; TCE: 21 mg/L; cis-DCE: 11 mg/L; 1,2- Dichlorobenzene: 15 mg/L; Benzene: 7 mg/L	Injection wells	nZVI (injected with powdered soy as an organ- ic dispersant (20% by mass); and also most batches incl palladium (1% by mass)	100 kg nZVI
USA, San Francisco, Hunters Point Ship Yard, US EPA 2016	Pilot	Three aquifers mentioned, un- clear which were tested	GW	TCE, DCE, VC		Injection (unspeci- fied method)	Uncertain (FRTR 2006 and Gavaskar <i>et al.</i> , 2005 report 40 tonnes of micro scale ZVI inject- ed)	
USA, Santa Maria, CA, US EPA 2016	Pilot	Interbedded sands, silts and clays (bedrock encountered)	GW	TCE, DCE	TCE (2.5 mg/L)		BNP	30g/L nZVI slurry - amount un- known
USA, Sheffield, Alabama, USA, US EPA 2016	Pilot	Unconsolidated sediments	GW	PCBs, PCE, TCE, DCE, VC	10,000 - 24,000 µg/L	Single injection point	Polysaccharide stabilized bime- tallic nanoiron	
USA, South Carolina, Former Manufacturing site (Chiang and Darring- ton 2014)	Pilot		GW	TCE		Direct push at eight points	nZVI (NANOFER)	~150 kg

Location and citations	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	NP Type	Amount Applied
USA, State College, Pennsylvania, Karn <i>et al.</i> , 2009 <i>Supplemental Material</i>				Pesticides (DDE, DDT)			nZVI	
USA, Titusville, PA, Karn <i>et al.</i> , 2009 <i>Supplemental Material</i>				PCE, TCE, cis-DCE			nZVI	
USA, Vandenberg Air Force Base (missile launch site), US EPA 2016	Pilot	Mixed alluvial layers: interbedded sands, silts, and clays	GW	TCE, DCE	TCE (2,500 µg/L)	Direct injection	Activated carbon impregnated with nano-scale porous metallic iron (BOS100®)	180 kg BOS100®,
USA, Winslow Township, New Jersey, US EPA 2016	Pilot	Unconsolidated sediments, Potomac-Raritan-Magothy sands, silty sands.	GW	PCE, TCE, DCE	TCE 3,000 µg/L	Gravity feed injection	nZVI	150 kg

## Notes:

- \* NanoRem pilot site
- \*\* Additional information supplied by AQUATEST A.S., Prague, Czech Republic
- \*\*\* Information from a web listing hosted by the University of Kentucky, USA:  
[www.ukrcee.org/Challenges/Documents/Groundwater/NP/Nano\\_Projects\\_IN\\_PLACE.pdf](http://www.ukrcee.org/Challenges/Documents/Groundwater/NP/Nano_Projects_IN_PLACE.pdf), Accessed January 2016
- \*\*\*\* July 2016, <http://reground-project.eu>, and Rainer Meckensck personal communication (University of Essen, Reground co-ordinator)
- \*\*\*\*\* Information supplied by Intrapore, Essen, Germany
- # Additional information supplied by Geoplano, Portugal, November 2016
- ## Additional information supplied by VEGAS, Germany, November 2016
- ### Additional information supplied by NANO IRON, s.r.o. Czech Republic,, November 2016

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