A Risk/Benefit Approach to the Application of Iron Nanoparticles for the Remediation of Contaminated Sites in the Environment

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EXECUTIVE SUMMARY

In the context of this report, unless otherwise specified, the term iron nanoparticles (NPs) refer to zero-valent (e.g. Fe(0)) as opposed to any of the oxidised nanoparticles of iron (e.g. Fe(II) or Fe(III) present in one or more forms of oxyhydroxides, carbonates, or other species).

In 2004, in a joint report, the Royal Society and Royal Academy of Engineering recommended a precautionary approach to the release of nanomaterials into the environment in the UK, which included a view that the free release of nanomaterials for environmental applications, such as remediation of groundwater, be prohibited until appropriate research has been undertaken to demonstrate that the benefits outweigh the potential risks. Since then, there have been evolutionary rather than revolutionary advances in the understanding of the benefits and potential risks from using iron NPs for the remediation of contaminated soil and groundwater. An increase in field trials, particularly in North America, has been accompanied by an exponential year-on-year increase in peer-reviewed papers on iron NPs and treatment efficacy of various contaminant types but a slower increase in papers studying the potential human health and ecological risks. Nevertheless, it is notable that of the research papers published, only a small percentage relate to field trials, and of those trials undertaken only 12% of those do not concern the treatment of chlorinated solvents. It would seem that the market has found chlorinated solvents to be a niche contaminant grouping where iron NPs are viewed as most effective, and potentially cost effective, against the alternative remedial treatment options presently available.

Iron NPs are a relatively new technology. However iron particles in the micro to millimetre scale have been used in remediation for over twenty years. NPs can have markedly different properties than larger chemically identical particles. This is in part both the opportunity for iron NPs and the cause of concerns over possibly different particle behaviour, fate and toxicity compared with their larger scale counterparts. As produced, most iron NPs tested fall into the 60-100 nm size range, although they rapidly agglomerate to form larger particles. However, practical field applications in the United States and Europe performed to date have typically used iron NPs in the order of 100 nm or more (in their primary non-agglomerated state).

When discussing the potential environmental and human health risks of the free release of iron NPs into the environment it is important to remember that iron is both an abundant element and an essential nutrient, but, like all substances, it can be toxic in excess. Furthermore, naturally occurring NPs containing iron are ubiquitous and manufactured iron NPs in the aqueous environment are generally believed to transform to various iron oxyhydroxides, similar in composition to these naturally-occurring iron oxide based materials. Two key risk appraisal questions are whether the properties of iron NPs cause appreciable risk during their use; and whether their end-products are sufficiently similar to natural iron oxyhydroxides so as not to represent a significant hazard. Published studies do not completely answer either question.

Iron NPs are highly reactive reducing agents and as such degrade organic compounds and change the oxidation state of elements. This, combined with potential catalytic enhancement of redox reactions, underlies their functionality in soil and groundwater remediation. It also underpins the presumption of their toxicity to living organisms. An interesting field scale observation has been the continued biological processes of dehalorespiration in chlorinated solvent contaminated groundwater treated with iron NPs, which indicates that microbial activity can continue even within the “aggressive” iron NP *in situ* treatment zone.

In practice, iron NPs are subject to two processes which reduce their effectiveness: agglomeration and passivation, both related to their high chemical reactivity. Iron NPs are attracted to each other and aggregate into larger, micro-scale particles, which in almost all cases reduces their mobility in water and their effective surface area. These micro-scale particles are then thought to behave in the same way as micro-scale zero-valent iron. Passivation results from the oxidation of iron NPs before reaching the contaminants they are intended to react with, through reaction with water, groundwater constituents such as nitrate and dissolved organic matter and the subsurface matrix. The general consensus in published studies is that passivated metallic nanoparticles have no significant cellular toxicity.

Unmodified iron NPs are rapidly filtered out through agglomeration and passivation processes. Depending on their modification, modified iron NPs may have increased persistence, enhanced subsurface migration and improved catalytic properties (or any combination of these). Modifications include coatings and doping with other metals. Iron NPs that have reacted in the treatment zone will end up as inert salts.

A concern is that unreacted iron NPs can spread from the treatment zones and cause harm to human health or the environment. Little information has been found about the modified iron NPs in practical applications. The available information suggests that iron NPs have relatively short lifetimes in the environment before they are inactivated (circa six months as a maximum) and migrate relatively short distances (100 metres) from injection points. However, the field scale evidence base is limited and potentially unreliable. Authoritative field scale observations of fate of iron NPs from remediation treatment points is recommended by this report.

Led by the USA and Canada, field scale applications of iron NPs for contaminated land remediation have already taken place in a number of developed countries with major research initiatives are underway in Germany and Spain. One or more major European funded projects are expected from late 2012, as evidenced by the EC's 2011 funding call 'FP7-NMP-2012-LARGE-6'. An unnecessarily restrictive view on risks of iron NP use in remediation would leave the UK at risk of falling behind other countries in the understanding, application and benefits of this remediation technology.

Most use of iron NPs has been for the treatment of aquifers contaminated by chlorinated solvents (mainly tetrachloroethene and trichloroethene). Such use competes with other remediation technologies such as *in situ* bioremediation, oxidation and reduction. While a "step change" in the possible scope of nano-remediation is foreseen by many of the exponents of nano-remediation in treating recalcitrant contaminants such as complex organics; this has yet to be achieved in practice and remains a laboratory scale and theoretical possibility. Therefore the immediate benefit of facilitating iron NP remediation is in allowing service providers to employ another tool for chlorinated solvent contamination problems, and perhaps improving the "climate" under which more innovative nano-remediation applications might develop.

The available evidence can support a range of interpretations about the potential risks from iron NP use in soil and groundwater remediation, some of which may differ from those reached by this report. From a regulatory and policy perspective this leaves an uncertain platform for decision-making. While suitable conditions *could* be put in place by regulators to allow iron NP use in remediation in the UK, such conditions are likely to be contentious as there is inadequate authoritative field scale observation of transport and fate of iron NPs in the subsurface, including the extent and reversibility of iron NP passivation and agglomeration. Providing authoritative field based trials, where iron NP

persistence and migration is observed and verified in practical situations would go a long way towards reducing this uncertainty.

Our recommendation is therefore the establishment of *interim* conditions for iron NP use in the field for the collection of the missing field scale information, with initial suggestions made in this report.

The literature contains a range of opinions about reputed iron NP impacts in the field. A structured expert elicitation workshop could be used to determine best and worst case scenarios for iron NP behaviour under field conditions. These can be used as the basis for probabilistic risk modelling to set interim conditions for field scale applications, as far as possible on the basis of a consensus opinion. These interim conditions could then be modified on the basis of ongoing observations of persistence and migration of iron NPs in the field.

Additionally, this report provides a range of prioritised supporting research suggestions which could also be tested through the same expert elicitation workshop. We believe that a prioritised research agenda is important to ensure that funding agencies achieve value for money from their research investment, and that gaps preventing the practical adoption of iron NP based remediation in the UK are addressed as a matter of urgency rather than more esoteric studies.

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1 INTRODUCTION

The UK has adopted a risk based approach to the management of historic land contamination in order to protect human health and the environment. The Model Procedures for the Management of Land Contamination (Defra and Environment Agency, 2004) provide a clear and consistent basis for the risk-based assessment, management and remediation of soil and groundwater contamination in England and Wales. The Model Procedures are predicated on the derivation of a conceptual site model (CSM) in which the spatial and temporal links between contaminant sources, pathways and receptors as well as associated uncertainties are identified. These *pollutant linkages* serve as the basis for the assessment of risks posed by the contamination and breaking these linkages sets the requirements for remedial action.

The use of iron particles in remediation is already well established. The treatment effect is based on particles of elemental iron acting as electron donors (a reducing agent) by being oxidised to iron (II) and iron (III), typically as a variety of oxyhydroxides, carbonates, etc. The iron particles used in environmental remediation applications are now commonly referred to as zero-valent iron (ZVI). A range of applications for ZVI have been devised within engineered *in situ* treatment zones, for example contained within the matrix of a permeable reactive barrier, or emplaced directly into a contaminated aquifer by direct injection. The smaller the particle size of the iron the greater the rate of reaction, and intuitively the greater the treatment effectiveness.

The term “nanomaterial” is now frequently used to describe a material with external dimensions, or an internal structure, at nanometre (10^{-9} m) scales that exhibits additional or different properties and behaviour compared with coarser materials of a similar chemical composition (Klaine *et al.* 2008). The use of iron nanoparticles (iron NP) is a relatively new approach to remediating certain contaminated soil and groundwater problems (US EPA 2008). In 1997 Wang and Zhang published a pioneering paper on the use of nano-scale ZVI particles. Their largely bench scale research showed that a range of processes operating at the nano-scale offered significant benefits for contaminated land remediation, and led to the use of iron NPs in the field for groundwater remediation at sites in North America and Europe (Otto *et al.* 2008, Karn *et al.* 2009, Müller and Nowack 2010). Within the UK, the use of any new substance (including iron NPs) for environmental remediation currently requires a licence from the relevant environmental protection agency (e.g. the Environment Agency in England and Wales), and, to date, no applications have been received for the use of iron NPs for this purpose.

A recent consultation across the European Union has shown that both experts and the general public see many benefits in the use of nano-technologies, and environmental applications are seen as having potential for “high benefits”. However, there are also concerns raised both by experts and the general public relating to the safety of nano-technology and its environmental impacts (European Commission 2010). From a regulatory point of view, there is no general, material-independent threshold below which “true” nano-scale properties are observed. Furthermore, the class of material that is seen as requiring regulatory attention is “particulate nanomaterial”, as many larger materials have internal structures at the nano-scale (European Commission JRC 2010).

In the UK the Royal Society and Royal Academy of Engineering published a report in 2004, *Nanoscience and Nanotechnologies: Opportunities and Uncertainties*. This report recommended a precautionary approach to the release of nanomaterials into the environment, which included a view that the free release use of nanomaterials for environmental applications, such as remediation of groundwater, be prohibited until

appropriate research has been undertaken to demonstrate that the benefits outweigh the potential risks. In 2008 the Royal Commission on Environmental Pollution reiterated many of the concerns of the Royal Society / Royal Academy report and identified a number of critical research needs to support the environmental regulation of nanomaterials. During the Belgian presidency of the European Commission, in October 2010, Paul Magnette, the Belgian Minister for Energy, Environment, Sustainable Development, and Consumer Protection proposed the obligatory product labelling and registration of all nanomaterials "on the market" EU-wide (European Commission 2010).

Over the course of this project the reviewers have been made aware of concerns about release of iron NPs for remediation in several other European countries: Austria, Spain and Switzerland, although it has been tested in the field and used in others, e.g. Czech Republic and Germany. At the time of writing, a European Commission project "Review of relevant environmental legislation for the regulatory control of nanomaterials" was underway. The review requires an understanding of the potential risks of nanomaterials to determine whether they are then adequately regulated. Provisional findings suggest that most Member States are still in the process of assessing existing policies, with little if any concrete legislative requirements (C. Ganzleben 2011 pers. comm.).

In 2010 Defra commissioned this review to determine whether there is now sufficient evidence to take a view on the balance of benefits versus risks for contaminated land remediation applications of iron NPs. CL:AIRE with r3 environmental technology ltd (r3, UK), University of Nottingham (UNOTT, UK), Deltares (The Netherlands), and Geosyntec (USA) were asked to carry out a desk study review to identify and outline the potential and known risks and benefits associated with the application of iron NPs for the remediation of contaminated soil and groundwater.

This review outlines the potential and known risks and benefits associated with the application of iron NPs for the remediation of contaminated soil and waters, and identifies where a net benefit is likely to exist, based on a review of the technical literature and existing iron NP based remediation case studies. It suggests key risk considerations to be taken into account when permitting the use of iron NPs for remediation, identifies significant gaps in knowledge and suggests how these might be overcome.

The research is timely and relevant given the increasing interest in the use of iron NP remediation technology, including by a number of international service providers operating in the UK. Related risk-benefit studies have been published in Belgium (OVAM 2006a and B), Switzerland (BAFU 2010), Quebec (Gouvernement du Québec 2006) and the USA (e.g. Karn *et al.* 2009). In addition, Germany is presently undertaking a risk benefit assessment (J. Frauenstein 2010 pers. comm.) whilst Austria is considering a risk benefit study (H. Kasamas 2010 pers. comm.)[1].

With a few exceptions, iron NP remediation technology is based on elemental (zero-valent) iron. This report therefore focuses on elemental iron nanoparticles, and wherever "iron NPs" are mentioned this refers to nano-scale zero-valent iron particles, and their modified forms. Emerging applications for iron oxide based nanoparticles are briefly discussed in Section 2.3.4.

[1] European status garnered from The Common Forum (2011). Quoted references in this paragraph are not in English but nevertheless included in the reference list.

1.1 Desk Study Approach

The technical literature search for this report has been developed from the articles found through Web of Knowledge, Google Scholar and Imperial College *MetaLib* searching journals published by *Wiley*, *Springer*, *ACS* and *Elsevier* (through *ScienceDirect*), as well as other references available on the internet.

A number of different search criteria were used to target different aspects of the use of iron nanoparticles necessary to cover all of the themes within the project specifications. The results of which were compiled in a spreadsheet and hyperlinked to the journal articles and their reference. The search criteria involved including papers from a small selection of internationally recognised experts in the field of iron nanoparticle research. The following search criteria were used:

- General: "nano", "iron" and " remediation";
- Field demonstrations – as above with the additional terms: "*in situ*", or "demonstration" or "field-scale";
- All papers by Professor Wei-xian Zhang of Lehigh University, Bethlehem, PA, USA;
- All papers by Professor Gregory Lowry of Carnegie-Mellon University, Pittsburgh, PA, USA;
- All papers by Dr Daniel Elliott;
- References from keynote papers.

For the general searches, results needed to be limited and were filtered by the impact rating of the journal in which they were published. For the general search on Google Scholar, once the papers were screened on impact rating, the results were cut off at 250. A total of 499 papers were compiled from the various searches. This report draws only upon the most useful of these various documents.

A further source of information was referrals, both from technical papers, and from international stakeholder networks and initiatives consulted over the course of this project. The international stakeholder networks and initiatives consulted included:

- CL:AIRE's Technology & Research Group (TRG) – CL:AIRE's independent expert technical panel
- Common Forum on Contaminated Land in the European Union (www.commonforum.eu)
- Consoil 2010 Session on (nano/microscale) iron based technologies (UFZ-Deltares/TNO 2010
- EUGRIS user-base and visitors (www.eugris.info)
- European Commission Directorate General for Research, the EU Joint Research Centre, and current DG Research funded projects
- Network for Industrially Contaminated Land in Europe (www.nicole.org)
- CABERNET, European Sustainable Brownfield Regeneration Network (www.cabernet.org.uk)
- US Environmental Protection Agency, including a joint webinar held with CL:AIRE and the project team on December 14th 2010 (which can be accessed via : www.clu-in.org/conf/tio/nano-iron/

These organisations also provided valuable information about recent case studies of the use of iron NPs in the field. In addition a small number of UK practitioners were canvassed for their views on the likely uptake of iron NPs for remediation in the UK, and the drivers and barriers to this including the balance of benefits to risks (see Annex 1).

The project team has subsequently read each of the 499 abstracts from the literature search, and categorised them to note if they comprise laboratory or field studies, and for which section of the report they were earmarked. Additionally the abstracts have been summarised to guide the team on the relevance and any particular interesting facets of the paper which may be picked out for the final report.

1.2 The UK Context for Contaminated Land Remediation

The UK has a comprehensive framework for dealing with the management of risks from land contamination (DoE 1994; Defra and Environment Agency 2004). In practice, slightly different legal regimes operate in each of the four countries that comprise the UK. For simplicity, mention of UK policy within this report refers to the situation in England unless otherwise stated. In the context of soil and groundwater contamination there are three key elements to risk management:

- A contaminant – a substance in, on, or under the land that has the potential to cause harm or pollution. The contaminant is also referred to as the source.
- A pathway - a route or means by which a receptor could be, or is exposed to, or affected by a contaminant.
- A receptor - something that could be adversely affected by a contaminant, such as people, an ecological system, property or a water body.

Each of these elements can exist independently, but they create a risk only where they are linked together – so that a particular contaminant affects a particular receptor through a particular pathway – the pollutant linkage.

Without a pollutant linkage, there is not a risk – even if a contaminant is present. Hence the process of remediation for mitigating risks (risk management) operates in one or more of the following ways: reducing or changing the source; managing contamination in the pathway or by protecting the receptor (for example by restricting land use). Figure 1 illustrates this pollutant linkage concept and the possible risk management interventions. Table 1 summarises available source management and pathway management remediation techniques.

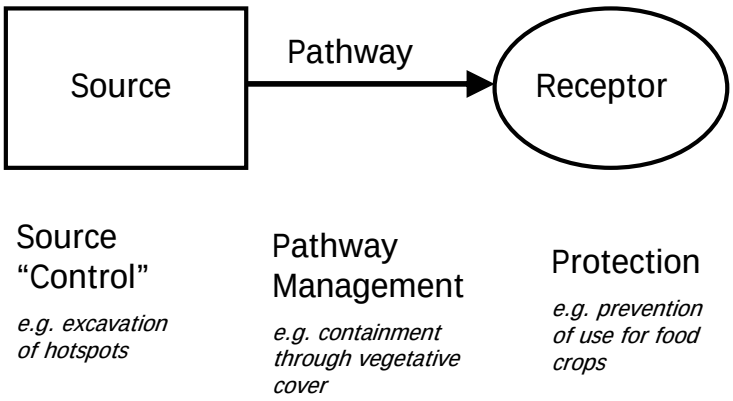

Figure 1 Components of a Pollutant Linkage where Actions Can Be Taken to Minimise Risk

The objectives set for any particular set of risk management interventions are therefore achieved by measures which either prevent migration along a pathway (for example containment using a barrier impermeable to groundwater movement) or reduce concentrations of contaminants monitored in soil and groundwater to levels that are judged not to pose a risk of significant harm to receptors. This judgment should be based on levels calculated for a particular site, commonly referred to as "site specific target levels". The target levels are based on a series of models and assumptions about how contaminants migrate through soil, water and air, (or via foodstuffs for human health), and so impact human health, water, ecology and/or buildings (Environment Agency and Defra 2004).

Table 1 Remediation Techniques Classified by their Role in Source and Pathway Management (summarized from Nathanail *et al.* 2007)

Medium	Source management	Pathway management
Solid phase	• Excavate and some form of *ex situ* treatment and/or landfill • Extraction process (based on moving air or water to recover contaminants from the soil, which also encompasses *in situ* heating and electro-remediation techniques) • Some form of *in situ* destruction applying biological and/or chemical treatments • Some form of *in situ* stabilisation to prevent migration of contaminants • Some form of *in situ* transformation to a less toxic form (e.g., Cr VI → Cr III) applying biological and/or chemical treatments	• Capping layers
Groundwater	• Mostly the source of the groundwater contamination ("source term") is a problem of a contaminated solid material, from which materials are dissolving into groundwater, or non-aqueous phase liquids (NAPLs) which have penetrated to the aquifer.	• Pump and treat, where contaminated water is captured and treated above ground • Containment using impermeable barriers • *In situ* treatment zones where groundwater is captured and treated *in situ* without above ground recovery (e.g. a permeable reactive barrier) • *In situ* treatment zones where volumes of groundwater and aquifer material are treated by extraction, degradation or stabilisation based treatments applied *in situ.* • Monitored natural attenuation
Vapour	• Mostly the source term is a problem of a contaminated solid material, from which materials are dissolving into groundwater, or non-aqueous phase liquids (NAPLs) from which vapours are being released.	• Containment using impermeable barriers • Extraction based processes • *In situ* destructive processes, in particular biodegradation • Natural attenuation

1.3 Using Iron Nanoparticles in Remediation

Iron NPs can be deployed for source management and pathway management interventions, as described in Table 2 and reviewed in Chapter 2. There are two broad types of intervention by which iron NPs can be applied to contamination problems *in situ*: by direct injection, or potentially contained *in situ* treatment applications such as the matrix of an engineered permeable reactive barrier. The vast majority of known *in situ* applications of iron NPs have involved direct injection techniques. A variety of direct injection approaches exist, but their basic aim is to introduce a slurry of iron NPs at a specific depth and in a specific amount directly into soil and/or aquifer materials, see Figure 2. While groundwater travel and diffusion account for onward migration of iron NPs *in situ* in many applications, more active transport mechanisms can also be used. These include the use of well infrastructure to enhance the gradient by introducing recirculation loops or pressurized injections (see Section 2.3). Direct injection may be applied via an engineered fracture in the subsurface created by an overpressure of water (hydrofracture) or air (pneumatic facture), see Figure 3. Fracturing is seen as advantageous for low permeability soils. Direct injection may be directed towards a source reduction application, but more commonly it is used in pathway management to create an *in* situ treatment zone for a defined volume of aquifer. A permeable reactive barrier is a system that captures the flow of groundwater *in situ* and directs the groundwater to some form of treatment, after which it continues to progress along the aquifer, see Figure 4. There are a range of configurations, from highly engineered Funnel and Gate™ configurations to injected "treatment walls".

Table 2 Source and Pathway Management Interventions Potentially Capable of Employing Iron NPs

Matrix	Application	Iron NP application
Subsurface solid phase	Source management *in situ*	<u>Direct Injection</u> • *In situ* redox degradation of organic contaminants • *In situ* redox transformation and sorption of inorganic contaminants
Groundwater	Pathway management *in situ*	<u>Direct Injection (including possibly via hydrofracture) in an uncontained *in situ* treatment zone</u> • *In situ* redox degradation of organic contaminants • *In situ* redox transformation and sorption of inorganic contaminants <u>Contained *in situ* treatment applications such as the matrix of an engineered permeable reactive barrier</u> • *In situ* redox degradation of organic contaminants • *In situ* redox transformation and sorption of inorganic contaminants <u>Integrated solutions</u> • Evidence supports possible synergies with *in situ* bioremediation or electro-remediation

Figure 2 - Direct Injection of Iron NPs in the Field at the Trenton Facility, New Jersey (Photo courtesy of Geosyntec Consultants)

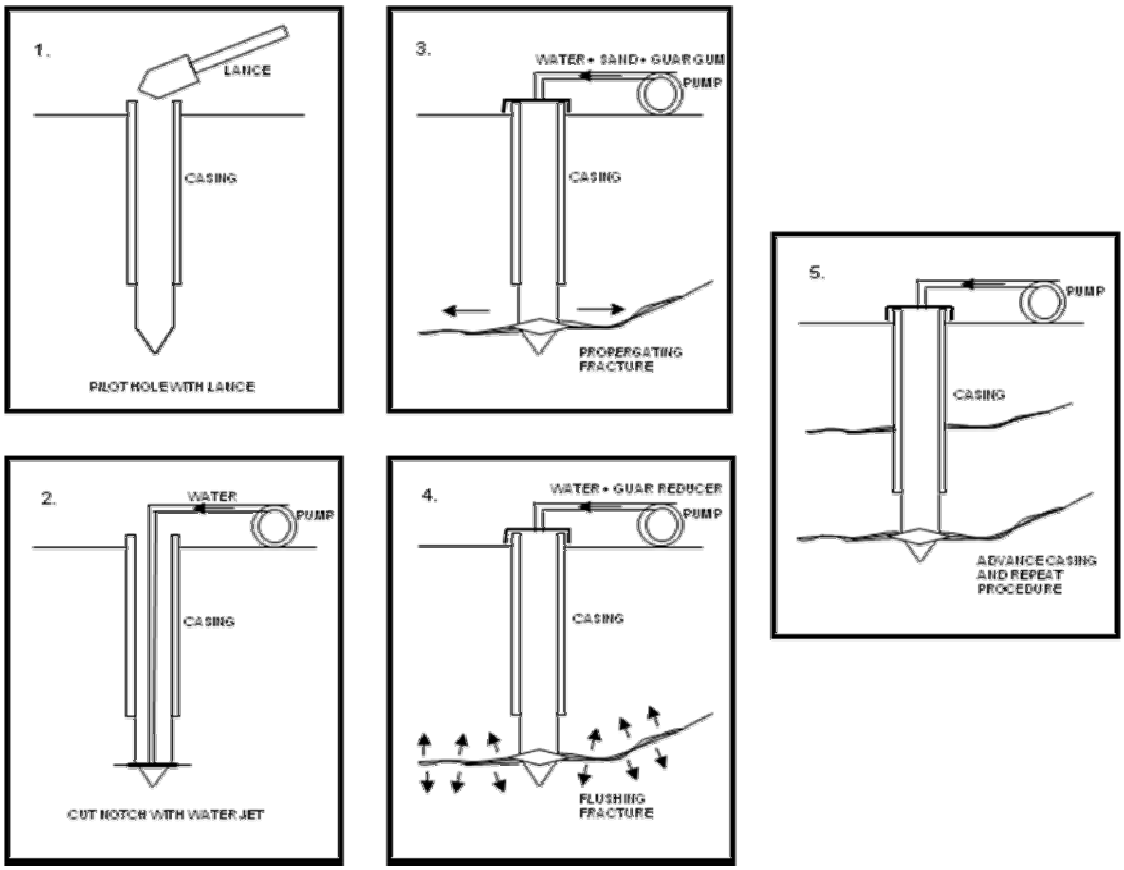

Figure 3 Hydrofracturing (after Schuring 2002)

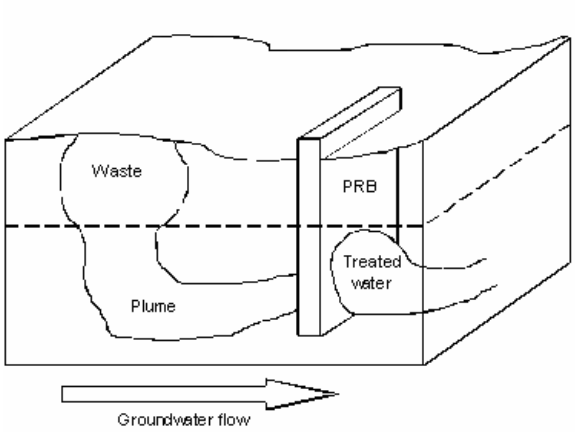

Figure 4 Typical PRB Configuration (from Nathanail *et al.* 2007)

The key to developing an effective remediation strategy is understanding how to apply most effectively source management or pathway management or both to breaking pollutant linkages. The conceptual model is an important means of understanding and presenting this rationale. A common misconception is to consider source management and pathway management interchangeably. For example the use of iron NPs [as a source management] is often presented as an alternative to a pump and treat system or to installing a permeable reactive barrier (PRB) [used for pathway management]. The implication is often made that the introduction of iron NPs is a "once and for all" treatment that removes the need for a longer term intervention such as a PRB or pump and treat, in a rather generic way. This is not strictly accurate because:

- Source management applications may not directly substitute for pathway management, for example the pathway management may be distant from a source and may be dealing with multiple sources
- The likelihood of any *in situ* source management intervention completely removing contamination from both the source and the residual plume is very low. Despite the possible improvements in redox performance achievable using iron NPs, their effectiveness in source removal is limited by a range of factors related to contaminant accessibility and availability, which is partially a function of the degree of mixing present and the quantity of contamination that is independent of the nano-scale processes occurring around any introduced iron NPs. These mass transfer-related deficiencies in the subsurface are a limitation typical of many *in situ* remediation technologies, not just iron NPs.

1.4 Comparing Conventional Zero-Valent Iron with Iron NPs for Remediation

Elemental or zero-valent iron (ZVI) is a reducing agent, which in the presence of an oxidising agent (i.e. a contaminant or reductate) serves as an electron donor to become Fe^{2+} and Fe^{3+}.

With the advent of nano scale ZVI, other forms of ZVI have come to be known as "micro" and "granular" ZVI, reflecting their particle sizes. None of these terms have formal definitions and are strictly related to the relative size of the ZVI particles produced. Microscale is used to refer to iron particles of 1-100 μm, or 10^{-6} to 10^{-4} m. Iron NPs refer to particles approximately 1 to 100 nm, or 10^{-9} to 10^{-7} m (Keane 2007). Practitioners believe that the agglomeration typical for iron NPs (see Section 4.5.2) means that under

field conditions particles are essentially transmitted through the subsurface at the "micro" scale or larger.[2] Active research is underway to evaluate the efficacy of various modifications to the iron NP whereby these new architectures may enhance stability in the subsurface and potentially improve reductate selectivity. However, field experience with surface-modified iron NPs is extremely limited and a detailed understanding of their performance or possible unintended consequences (i.e. transport beyond desired treatment zones, etc.) is not attainable at this juncture without additional research.

Use of iron as a redox agent in remediation has an established track record for the *in situ* pathway management of a wide range of contaminants in groundwater since its first application at the Canadian Air Force base at Borden (Gillham and Burris 1992, Gillham and O'Hannesin 1994, O'Hannesin and Gillham 1998). Initially pulverised iron (e.g. filings or turnings) was used in permeable reactive barriers based on the Funnel and Gate™ concept, developed at the University of Waterloo (Starr and Cherry 1994). By 2005 around 120 ZVI PRBs had already been installed worldwide (ITRC 2005a), with over 90 in the USA.

Microscale ZVI has also, but less frequently, been applied as an *in situ* treatment agent by direct injection (e.g. Chen *et al.* 2008, Shackelford *et al.* 2005, Wadley *et al.* 2005) although direct injection can be difficult to accomplish because of the handling properties of the ZVI / water slurries which are difficult to pump and penetrate soil relatively poorly (Uyttebroek *et al.* 2010). ZVI has also been considered as an *in situ* stabilisation agent for a range of potentially toxic elements (Cundy *et al.* 2008, Li *et al.* 2006a), for example arsenic or chromium (VI). Steel shot has been tested for *in situ* stabilisation of trace elements (Ruttens *et al.* 2006). In these applications the reduced species is ultimately sorbed to iron (III) oxides / hydroxides formed by the oxidation of the ZVI (Cao *et al.* 2006).

However, *in situ* chemical oxidation (ISCO) treatment systems using iron have played a wider role in source management where the redox process is based on Fenton's reagent (see Box 1).

Other types of zero-valent metals on their own or in mixtures with iron have been tested for the degradation of chlorinated solvents and also reduction of chromium (VI), at least at laboratory scale, for example, zero-valent copper, zinc or nickel (Cheng *et al.* 2010; Rivero-Huguet, and Marshall 2009; Sarathy *et al.* 2010, Zhang *et al.* 2007). However, these have not generally been used in practical remediation projects. Zero-valent magnesium, a very powerful reductant (Mg^o -2.37 V vs -0.44 V for Fe^0), is being explored for *ex situ* applications in the destruction of especially recalcitrant contaminants such as polychlorinated biphenyls (PCBs) (Birke *et al*., 2009). However, metals like Mg^0 react vigorously with water and likely would not be deployed for *in situ* treatment of contaminated groundwater.

[2] For example, as discussed in the December 2010 US EPA webinar *Field scale Remediation Experience using Iron Nanoparticles and Evolving Risk-Benefit Understanding*, accessible from: http://www.cluin.org/live/archive/

Box 1: *In situ* Chemical Oxidation (ISCO) using Fenton's Reagent (ITRC 2005b)

In situ chemical oxidation refers to the addition of oxidation agents into the subsurface. Oxidants are injected directly into the subsurface, mixed with a catalyst and injected, or combined with an extract from the site, injected and re-circulated. Typically, these ISCO agents form a homogeneous treatment system. ISCO can be carried out as a source management treatment or for pathway management. Where ISCO is used for source management the effect of application is typically aggressive, and Fenton's reagent is a commonly employed oxidant. Oxidation using liquid hydrogen peroxide (H_2O_2) in the presence of native or supplemental ferrous iron (Fe^{2+}) produces Fenton's reagent, which yields free hydroxyl radicals ($OH^{\bullet}$). These oxidants are very effective at low pH (3–5).

Other chemical oxidation agents used in the treatment of chlorinated solvents include persulphate and permanganate (Tsai *et al.* 2008).

2 THE CURRENT STATE OF THE ART

2.1 Production and Effectiveness of Iron NPs

A range of iron NPs have been produced using a variety of methods and tested at least at bench scale. Wiesner *et al.* (2006) report that in general, two iron NP synthesis methods are used commercially: bottom-up and top-down approaches. The bottom-up approach begins with dissolved iron in solution and uses a reductant to convert dissolved metal to nano ZVI (nZVI). The top-down approach begins with micrometre to millimetre-sized iron filings, which are ball-milled to fine, nano-sized particles. Most of the following are "bottom up" processes involving the formation of nano-scale iron from smaller or dissolved iron-bearing constituents.

1. The first method to be developed involves the reduction of aqueous iron salts (typically ferric chloride (Wang and Zhang 1997, Zhang *et al.* 1998) or ferrous sulphate (Elliott *et al.* 2008) by sodium borohydride). The nZVI particles typically produced are in the range 10-100 nm with a mean size of 50 ± 15 nm and a specific surface area of 10-50 m^2/g. There are several ways of achieving this which are reviewed by Lien *et al.* (2006).
2. Nanoparticles may also be formed by heating iron pentacarbonyl to 200-250°C (Karlsson *et al.* 2005). At this temperature it will disassociate into nZVI and carbon monoxide. The nanoparticles formed in this reaction are approximately 5 nm.
3. Reacting iron oxides with hydrogen will produce larger particles, in the size range of 200-300 nm. (Li *et al.* 2006b). Acid digestion at near-room temperature produces particles with an average particle size of 20 nm, or 5 nm if carried out in the presence of a surfactant (Azad 2007).
4. Iron NPs can be crystallised by gas phase reduction of FeOOH [3] producing particles with an average size of 70 nm and a surface area of 30 m^2/g.
5. Iron NPs can also be produced from nano-scale ferrihydrite (Fe_2O_3) $0.5H_2O$ [4]. This product has an average particle size of 50 nm (range 20-100 nm) and a surface area of around 25 m^2/g, and may be coated with a biodegradable organic and inorganic stabilizer to aid dispersion.
6. Iron NPs may also be produced by physical methods including condensation and also milling and attrition processes (Li *et al.* 2006b, Wiesner *et al.* 2006). A number of research groups and major remediation practitioners (e.g. Golder Associates) are using "top-down" processes to produce nano-scale iron from microscale feedstock through the use of sophisticated ball mill technology.
7. Tiehm *et al.* (2009) describe the production of "air stable" iron NPs ultrasonically by applying ultrasound to a solution of $Fe(CO)_5$ in edible oil. The resulting iron nanoparticles were dispersed in a carbon matrix, and coated with a non-crystalline carbon layer of approximately 2.5 nm.
8. Li *et al.* (2006b) describe a range of additional production methods based on chemical processes that have been used at laboratory-scale, including electrodeposition.

[3] http://www.todaamerica.com/products/products.html

[4] http://www.nanoiron.cz/en/nanofer-25

Many of the above referenced synthetic methods were not devised with sustainability-related considerations as primary factors. Research is underway to evaluate alternative synthetic or manufacturing routes which may be safer, use less energy, or yield more overall sustainability enhancements. In fact, the use of iron (II) sulphate as a starting material in the borohydride synthetic process was the result of a desire to increase iron NP production efficiency (e.g. only having to reduce Fe(II) to Fe(0) as opposed to Fe(III) to Fe(0), and to enhance safety.

The iron NP manufacture market is highly fragmented. There are several commercial manufacturers of nano iron each using a proprietary synthesis method. Most iron NP product vendors are small entities, but exceptions include Toda Kogyo Group (Japan) and BASF. All are reluctant to release figures on the volume of their iron NP business. Anecdotal evidence suggests that the current size of the iron NP market, including manufacturing and sales, is in the order of 4,500 kg/year. Toda is a major worldwide producer of iron oxides used in the manufacture of pigments, cathodic materials, and magnets. Their commercial iron NPs business, through subsidiary Toda America Inc., represents a small fraction of their overall businesses. For example, iron NPs find applications in the food sector, medical sector and for water purification (Chaudry and Castle 2011, Lewinski *et al.* 2008, Saji *et al.* 2010). The current size of the iron NP market for remediation is still fairly limited.

Table 3 sets out typical optimal performance ranges for iron NPs. A range of modifications may be employed to alter these optima as described below. Table 4 sets out the typical range of contaminants and matrix materials so far treated at a practical scale by iron NPs based on the case study information summarised in Annex 2. Together these provide an initial and rudimentary “operating window” for iron NPs as a remediation technology. However, the potential applications for iron NPs based on bench and pilot scale research is wider, and this report discusses both the applications which have been practically realised, and those which research indicates are potentially available. The report clearly indicates where outcomes are supported by evidence from field scale applications.

Table 3 Optimum Conditions for Iron NP Performance (Cook 2009, Keane 2009, Li *et al.* 2006a)

Groundwater condition	Optimum Conditions
Dissolved oxygen	Ideally less than 2 mg/L
Oxidation reduction potential	Preferably under anaerobic conditions Greatest reactivity ORP =< -400 mV
pH	Effective below pH ~ 8 Preferred pH range from 5-7
Permeability	Hydraulic conductivity on the order of 10^{-5} m/s or better (Interventions such as fracturing have been suggested to improve performance in low permeability media)

Table 4 Treatable Contaminants and Matrices for Zero-Valent Iron NPs based on Field Scale Applications.

APPLICABLE Contaminants and materials – *Outcome: destruction or stabilisation*								
Organic	Halogenated volatile	✓✓	Organic	PCBs	✓	Inorganic		
	Halogenated semivolatile	✓✓		Pesticides/herbicides	?		Cyanides	?
	Non-halogenated volatile	?		Dioxins/furans	?		Corrosives	?
	Non-halogenated semivolatile	?	Inorganic	Volatile metals	?	Misc	Asbestos	*x*
	Organic corrosives	?		Non-volatile metals	✓		Oxidisers	✓
	Organic cyanides	?		Radionuclides	?		Reducers	?
Gravel – >2mm	Sand – 0.06 to 2mm		Silt – 2 – 60µm		Clay – < 2µm		Peat	
✓✓	✓✓		?		?		?	
Key: ✓✓ Usually applicable; ✓ Likely applicable; **?** May be applicable; ***x*** not treatable; ***x x*** may worsen situation.								
Notes PRB configurations, or possibly introduction in fracture zones may be applicable for low permeability aquifers Laboratory based studies indicate that potentially the range of contaminant types is wider than currently achieved in the field (see Table 5)								

2.2 Iron NP Enhancements

Laboratory scale studies indicate that zero-valent iron NPs can remain active in soil and water environments for periods in the order of 6 – 8 weeks (Zhang 2003). However, more recent research indicates that the reactive timeframe may be longer, approximately 6 months or so for specific modifications of iron NPs (Phenrat *et al.* 2009a). In practice, nZVI particles are subject to two processes which reduce their effectiveness: agglomeration and passivation, both related to the high chemical reactivity of the iron NPs. Iron NPs are attracted to each other and aggregate into larger particles, which in almost all cases reduces their mobility in water and their effective surface area. Passivation results from the oxidation of iron NPs before they reach the contaminants they are intended to react with. Passivation results from the formation of an exterior oxidised layer, the composition and chemistry of which is a function of the site specific redox and geochemical conditions. The layer results from reactions with the groundwater itself, target contaminants, or other redox-amenable constituents such as dissolved organic matter or ions such as nitrate. Water will be the dominant material present, and since this is also reduced by iron NPs, it can be anticipated that at least some proportion of the reducing capacity of the iron will be consumed by reactions with water itself. A number of modifications are introduced to improve the effectiveness of iron NPs by reducing the scale of agglomeration and the immediacy of passivation, as described below. Other modifications discussed below, include doping with other metals to improve reactivity and suspension in emulsions to better access free-phase NAPL. Modifications which have been developed include (Parbs and Birke 2005, US EPA 2008):

- Stabilisation using coatings and structures with other compounds e.g. in Phenrat *et al.* (2008)

- Bimetallic nanoparticles (BNP) e.g. in Kim *et al.* (2008), Quinn *et al*. (2009) which typically utilize small quantities (i.e. <1% by weight) of other metals (e.g. palladium, platinum, etc.) to serve a catalysts
- Emulsified nZVI (eZVI) e.g. in O'Hara *et al.* (2006)
- Anchored iron NPs e.g. in Ponder *et al.* (2001)

The addition of different substances and materials (for example organic compounds as coatings, or small amounts of potentially toxic elements in BNP) has a bearing on the risks inherent in iron NP use (discussed in Section 2.2.2).

The majority of field scale use of iron NPs has used unmodified iron NPs (Li *et al*., 2006). However, interestingly, iron NPs can develop a coating from dissolved organic matter after release into an aquifer. This has been shown to increase particle mobility (Phenrat *et al.* 2009b). Johnson *et al.* (2009) tested stabilisation with "natural organic matter" at solutions of 20 and 2 mg/l in laboratory columns and concluded that naturally occurring organic matter could offer a useful degree of nZVI stabilisation in injection zones. Conversely, humic substances may also depress iron NP activity against organic contaminants (Lee *et al.* 2009; Zhang *et al.* 2009).

2.2.1 Stabilisation

In order to be functional under field conditions introduced iron NPs need to have properties that allow the development of engineered remediation processes. Foremost amongst these are a reasonable and known persistence (or half life) in the environment as an active treatment agent; depending on the type of application, an ability to move through aquifers from injection points for a useful and predictable distance; and a treatment effect that is primarily delivered to target contaminants rather than in a non-specific way in the subsurface. Therefore stabilisation interventions are primarily those that control the reactivity of iron NPs in a known way so that they do not adhere to each other (agglomerate) in a way that restricts their movement in the subsurface and do not sorb to soil surfaces within a short distance of their injection point. These are all outcomes that rapidly affect unmodified iron NPs.

The properties desired depend strongly on the type of remediation taking place. For PRBs it is not necessary to ensure mobility, and indeed anchored iron NPs may be beneficial. However, it is important to maximise the operational life time of the iron NPs as groundwater flows through the PRB so that the PRB does not have to be recharged with new iron NPs on an unacceptably frequent basis. In addition, within a PRB the groundwater "brings" contaminants to the treatment matrix, so as long as the matrix components are stable with respect to each other, there is a lesser concern about non-specific reactions using up the redox capacity added by the iron NPs.

On one hand, it might be desirable for nZVI deployed into source areas to remain close to the points of injection; that is, for relatively limited movement to occur. On the other hand, it may also be important to ensure that iron NPs are able to travel at least tens of metres through the subsurface over time and still deliver a useful treatment effect, to avoid the cost of very closely spaced injection points. In this kind of a system non-specific losses of redox capacity may be an important consideration, and a major design concern may be devising how to avoid NPs being sorbed / deactivated on soil surfaces, while still being reactive enough to treat contaminants.

For both PRBs and injection based systems the key trade-off taking place is:

- The benefit of using more reactive treatment agents (iron NPs) which may require more difficult engineering, more difficult production and more frequent application, versus
- Using less reactive conventional ZVI which can be dosed in larger amounts, is cheaper and has a longer lifetime in the subsurface, but is less reactive so conceivably treats less contaminants per unit time, and a narrower range of contaminants.

Seen from this perspective the importance of a good site conceptual model that considers the *flux* and *range* of contaminants passing through a pathway management system is a key determining factor (along with materials costs) in making a choice between iron NPs and conventional ZVI.

A number of bench scale investigations on coatings have been carried out (Keane 2009) which have tested a range of approaches:

- Hydrophilic (biodegradable) biopolymers such as starch, guar gum, alginate, and aspartame (He and Zhao 2005; Tiraferri *et al.* 2008; Saleh *et al.* 2008; Tiraferri and Sethi 2009; Bezbaruah *et al.* 2009a)
- Carboxymethyl cellulose - CMC (He *et al.* 2007; Phenrat *et al.* 2008)
- Chitosan (Zhu *et al.* 2006; Geng *et al.* 2009)
- Natural organic matter such as humic acid (Xie and Shang 2005; Zhu *et al.* 2008)
- Polyelectrolytes such as polyacrylic acid, poly(methyl methacrylate), ion-exchange resins, and block copolymers (Kanel and Choi 2007; Zhao *et al.* 2008; Sirk *et al.* 2009, Wang *et al.* 2010)
- Amphiphiles including various surfactants, which can be anionic, cationic, or non-ionic (Hydutsky *et al.* 2007; Kanel *et al.* 2007; Zhu *et al.* 2008) and block copolymers (Saleh *et al.* 2005, 2007, 2008).

The intention of the modification has generally been to impart greater mobility potential for the surface modified irons. Surface modified iron exhibits greater stability in bench-scale batch studies. While the surface architecture is intended to persist for a while, it seems likely that it will eventually be degraded or detach. The carbonaceous content of the surface architecture may also eventually serve as a microbial substrate (electron donor). Polyelectrolyte modified nZVI have been found in laboratory studies to retain improved mobility in sand columns for considerable periods. A range of polyelectrolytes were tested which reduced agglomeration and maintained mobility for the modified nZVI over many months (Kim *et al.* 2009).

Surface modification can also add different functional groups or structural units to the base iron to provide a variety of performance enhancements. While the groups bonding to the iron surface are usually hydrophilic (e.g. carboxyl), other structural attributes may be added, for example, to selectively permit transfer of chlorinated solvents to iron NP active sites (Phenrat *et al.* 2009b). Another example is the possibility that iron-NPs stabilised with chitosan might have improved functionality in reducing chromium (VI) because the chitosan complexes the iron (III) and chromium (III) produced (Geng *et al.* 2009).

Surface modified irons have been evaluated extensively in the peer-reviewed literature over the past few years but there are very few field applications (e.g. Saleh *et al.* 2005). Aquifer injection tests indicate that even stabilised iron NPs are rapidly immobilised *in situ*. For example, Bennett *et al.* (2010) found that CMC stabilised iron NPs were immobilised within 13 hours.

2.2.2 Bimetallic Nanoparticles (BNPs)

The aim of including additional metals in iron NP formulations is to increase reactivity by catalysis and serve as hydrogenation catalysts. Palladium (Pd) has been used in Fe/Pd bimetallics and is a widely used hydrogenation catalyst in a wide variety of organic chemistry syntheses. An important objective of this increased reactivity is to promote complete conversion of organic pollutants to harmless compounds without the release of toxic intermediate breakdown products, for example, converting trichloroethylene (TCE) to ethane without a build up of the highly toxic intermediate product, vinyl chloride (Nutt *et al.* 2005). For the chloroethenes, the catalyst (Pd typically), increases the reaction rate as compared to bare nZVI. The power of the Fe/Pd bimetallic system is in the treatment of more recalcitrant contaminant classes such as the chlorinated benzenes or PCBs. While comparatively slow, Fe/Pd can degrade the higher chlorinated benzenes as compared to negligible success with bare nZVI or conventional ZVI (Zhang *et al.* 1998, Zhu & Lim 2007, Zhu *et al.* 2008, Shih *et al.* 2008).

Iron NPs containing Pd are commercially available and currently the most common BNP. Pd has been added in small amounts (doped), for example, by soaking fresh iron NPs in an ethanol solution with palladium acetate. This promotes the reduction and precipitation of Pd on the iron surface (Wang and Zhang 1997). Other BNPs can be produced in similar ways, including Fe/Ag, Fe/Au, Fe/Co, Fe/Cu, Fe/Ni and Fe/Pt (Xu and Zhang 2000). In laboratory studies, the redox reaction kinetics, and consequently contaminant degradation rates, are usually found to be increased for BNP in comparison to nano or micro iron (Zhang and Elliott 2006) due to the catalytic effect of the secondary metal (Tratnyek and Johnson 2006). A less toxic Fe/Pd production method uses non-toxic ascorbic acid and sodium carboxymethyl cellulose (CMC) as a reducing and capping agent (Liu *et al.* 2009).

2.2.3 Emulsified Iron NPs

Emulsified ZVI (eZVI) was developed by NASA and collaborators including the University of Central Florida, Geosyntec Consultants, Battelle Memorial Institute, and US EPA with the intention of creating a source management remediation technology for a range of primarily dense non-aqueous phase chlorinated solvents (Quinn *et al*. 2005). Dense non-aqueous phase liquids (DNAPLs) such as pure trichloroethene (TCE) or carbon tetrachloride (CT) are common groundwater contaminants and are notoriously difficult to remediate because of mass transfer-related accessibility issues, their specific gravity which exceeds that of water, and their tendency to serve as long-term sources of contamination. A feature of DNAPLs is their ability to form pools or pockets in the subsurface within and below aquifers depending on the stratigraphy of the subsurface as illustrated in Figure 5.

The eZVI technology uses either nano-scale or micro-scale iron and entails the use of a food-grade surfactant, a biodegradable vegetable oil, and water which form emulsion particles or droplets that contain the aqueous iron particles surrounded by an oil-liquid membrane (Quinn *et al.* 2005). A schematic of the eZVI structure is shown in Figure 6. The exterior of the oil membrane of eZVI exhibits similar hydrophobic properties as the source area DNAPL contaminants. The principal mechanism for the eZVI process is as follows (Quinn *et al.* 2005): (1) the eZVI is miscible with DNAPL areas meaning that contaminants can diffuse into the eZVI hydrophobic oil-liquid membrane, (2) contaminants then diffuse into aqueous interior where contact with the iron can occur, and (3) elevated concentrations of by-products (presumed to be non-halogenated hydrocarbons) from the dehalogenation reactions (either reductive dehalogenation, beta-elimination, or both) result in a gradient helping to expel these materials. The hydrophobic oil membrane also protects the interior iron from groundwater inorganic constituents that could otherwise

consume reducing capacity (Quinn *et al.* 2005). The principal advantage of this technology is its potential for use in directly treating source areas.

A limitation for iron NPs as a source zone treatment for DNAPLs is that they deliver their treatment effect only at the interface between the groundwater and the NAPL. The destruction of the DNAPL therefore can take too long to be practical as a source management intervention.

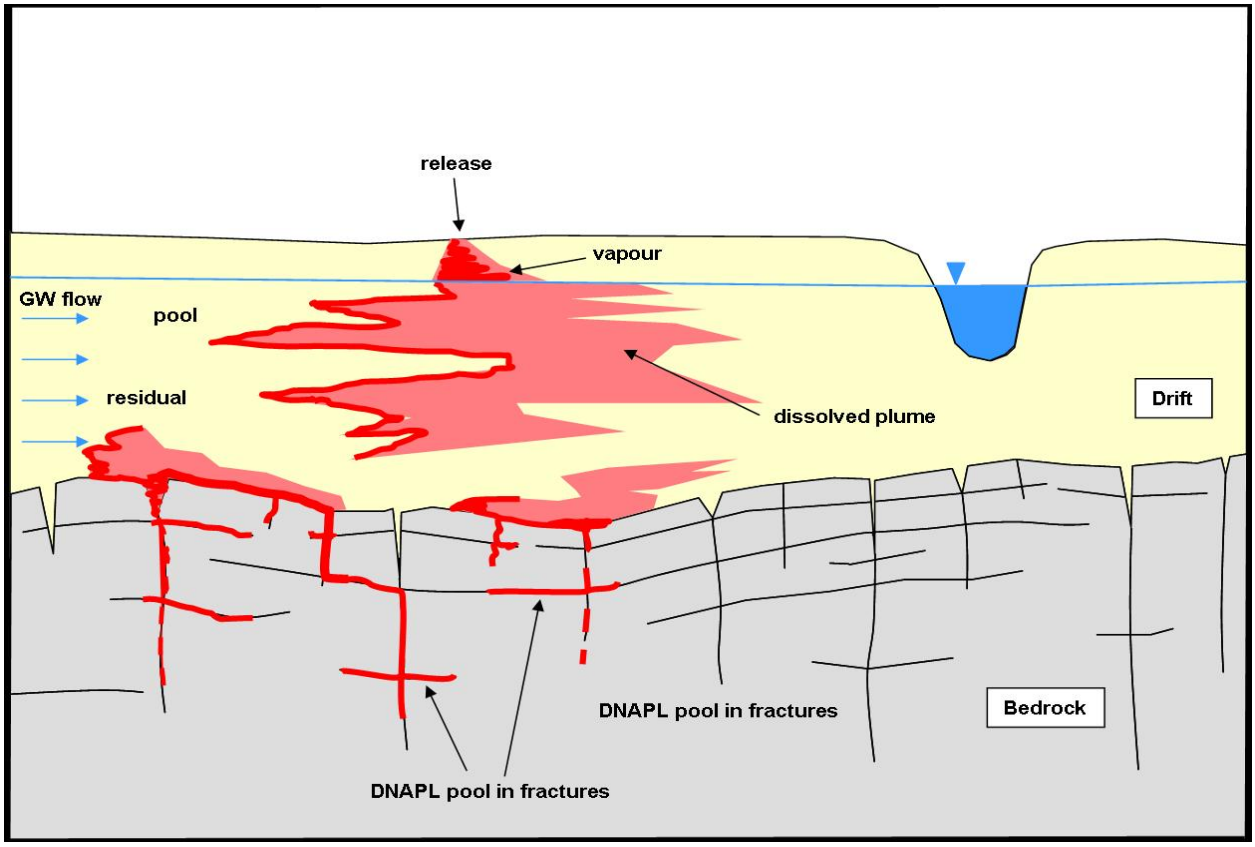

Figure 5 DNAPL Problem Illustration based on Pankow and Cherry (1996)

Laboratory studies have indicated that a more stable and reactive emulsion can be produced with smaller iron particles (Geiger *et al.* 2002). The emulsified oil membrane is made up of biodegradable vegetable oil and food-grade surfactant. Natural degradation of the oil and surfactant also enhance biological activity, which contributes further to the degradation of the contaminant both in the DNAPL and dissolved phase (Quinn *et al.* 2005), leading to significant reductions in TCE concentrations in soil and groundwater associated with an increase in reaction products (cis-DCE, VC) during the first field scale trial using eZVI at Cape Canaveral, Florida. eZVI using iron NPs has been demonstrated at the Parris Island Marine Corps Recruit Depot in South Carolina, USA (ESTCP 2010) following pilot scale tests at Cape Canaveral Air Force Station, Florida, USA (O'Hara *et al.* 2006).

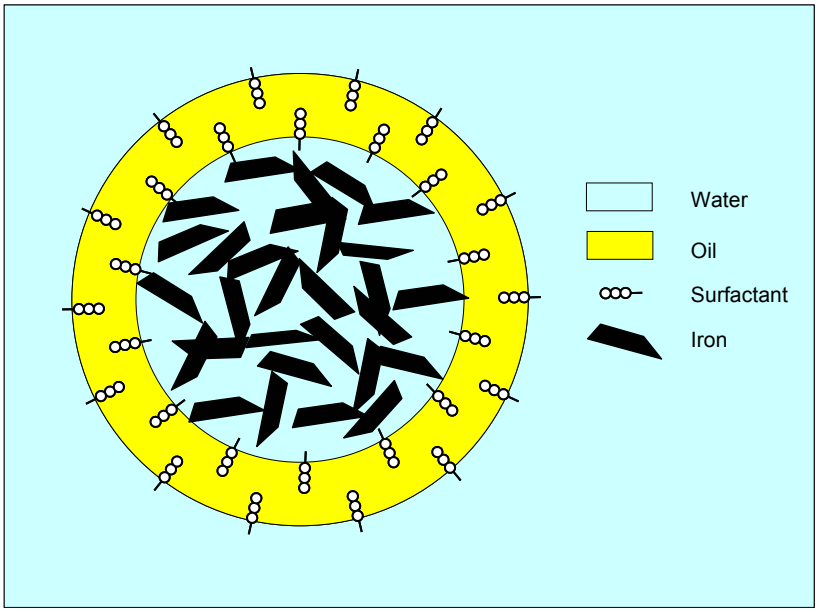

Figure 6 Schematic of Emulsified eZVI Droplet showing the Oil-Liquid Membrane Surrounding Particles of ZVI in Water. After Quinn *et al.* (2005).

2.2.4 Anchored Iron NPs

Research has been carried out to assess the feasibility of supporting iron NPs and BNP on carbon, cellulose acetate, polymeric resin or silica to prevent agglomeration and aid dispersion of the iron NPs (Ponder *et al.* 2000, 2001, Schrick *et al.* 2002, Zheng *et al.* 2008, Wu and Ritchie 2008). The enhanced reactivity and passive corrosion behaviour of these materials should make them good candidates for use in permeable reactive barriers and for injection into groundwater plumes. Zheng *et al.* (2008) also suggest that for their iron NP and silica formulation, surface silanol groups can be modified with organic functional groups to enhance remediation performance, for example sorption of dissolved NAPLs from water.

The use of carbon NPs as a support medium has also been researched in Germany. The carbon platelets are 50–200 nm in diameter (Parbs and Birke 2005). The hydrophobic nature of the composite, high mobility, and combined sorbent and reductant properties indicate this to be a promising material for the degradation of chlorinated aliphatics (Müller and Nowack 2010). The same team has developed a product called “carbo-iron” which has “iron nano-clusters” embedded on finely divided activated carbon (particle size circa 800 nm). The carbon formulation is intended to allow better transportation as a colloid, and also to sorb hydrophobic contaminants to the vicinity of the “iron nano-clusters” (Mackenzie *et al.* 2008).

2.3 Application of Iron NPs to Remediation

The first demonstration of iron NPs in the field was carried out using Fe/Pd BNP applied at a manufacturing site in Trenton, New Jersey, USA. The initial pilot test at Trenton in 2000 (Elliott and Zhang 2001), was conducted in an volume of 3 m x 4.5 m over a saturated thickness of 6 m, and was followed by larger-scale injection in 2003 and then the full demonstration in 2007 where 224 kg of nZVI was injected into two distinct hotspots (Elliot 2010). Since then a significant body of experience has developed both in terms of bench scale technology development, and applications in the field (Gavaskar *et al.* 2005, Karn *et*

al. 2009). In 2005 15 field scale applications of iron NPs and BNP were known to the US EPA (Watlington 2005, Kovalick 2005). By September 2008, there were data for a total of 26 sites where iron NPs had been applied in the field (US EPA 2008) and in 2009 projects had been reported at 44 sites in seven countries: USA, Canada, Germany, Czech Republic, Italy, Slovakia and Taiwan (Karn *et al.* 2009). This study has identified 58 actual field-scale applications reported in the academic literature. It is likely however, that there are numerous other field-scale applications as yet unreported in the literature. Despite the vast number of relevant papers discussed in Section 1.1, only about 10% of the pre-screened relevant papers refer to actual demonstration, or field case studies. Annex 2 collates the key information available from field studies reported in the literature to date.

The published case studies indicate that North America, and particularly the USA has the largest number of practical applications of iron NPs in the remediation of soil and groundwater. One field application was also recorded in Taiwan, the only field study collated within Asia. Field applications are now being undertaken in Europe through major research investments because of the anticipated advantages of high reactivity and catalytic properties of iron NPs, most notably in within Germany and the Czech Republic. Recognising the slower rate of uptake in Europe, the European Commission Directorate of Research has now issued a major call for proposals for 'large scale integrated projects' to promote the exploitation of nano scale processes in remediation[5]. Laboratory studies are much more broadly distributed internationally. A number of ongoing collaborative research projects are being supported at an EU level including UPSOIL; CITYCHLOR (EC Framework 6 Projects); NanoHouse; Nanopolytox; Nanosustain; and Nanofate (EC Framework 7 Projects).

Commercial grade (0.57-2 mm diameter) macro zero-valent iron filings were used for the first UK, and indeed first European, application of ZVI. This took place at the former Nortel Network site in Northern Ireland (CL:AIRE, 2001). However, no field applications of iron NPs have yet taken place in the UK, although it is notable that iron nanoparticles have been deployed in the UK for treating waste effluents (not a soil and groundwater system) at Aldermaston (Dickinson and Scott 2010). A number of UK universities are undertaking iron NP research including the University of Oxford, University of Greenwich, Bristol University, University of Brighton and Cranfield University, with many of the PhDs linked up with UK industrial partners. The views of a number of UK practitioners (summarised in Annex 1) indicate that some service providers believe that they will use iron NPs within the next three years, although none have iron NP projects which are imminent.

Through reviewing the literature there appears some disparity between the potential usefulness of iron NPs determined in bench scale experimentation, and what has been tested at a field scale or implemented in practical remediation projects. There are two broad types of differences. The first is the range of treatable contaminants (which is discussed in more detail in Section 3.1), and the second relates to the engineering of interventions to actually apply iron NPs to contaminants *in situ* be it via direct injection or in a PRB.

[5] 'FP7-NMP-2012-LARGE-6', incorporating '*NMP.2012.1.2-1* Nanotechnology solutions for in-situ soil and groundwater remediation'. Available at: http://ec.europa.eu/research/participants/portal/page/cooperation?callIdentifier=FP7-nmp-2012-large-6

This report takes a pragmatic view of the state of the art, discussing what is taking place at a field scale now and what might conceivably be possible. The focus of the state of the art discussion is on applications for pathway management via direct injection or PRBs, direct injection for source management applications and novel ideas for iron NP use in particular integrated approaches with other processes such as biodegradation. In practice this focus on field scale use also means a more limited range of treatable contaminants and taking account of a number of practical difficulties encountered in iron NP use.

2.3.1 Pathway Management Applications of Iron NPs

2.3.1.1 Via Direct Injection

Iron NPs are usually applied to contaminant sources or groundwater plumes using direct injection methods, either gravity-fed or under pressure. Iron NPs are typically supplied in a liquid slurry, both to ensure a stabilised and active iron NP product, and because the introduction of iron NPs into the subsurface requires their suspension in some form of a slurry (Henn and Waddill 2006, Müller and Nowack 2010, Comba *et al.* 2011). Iron NPs can be suspended in a variety of fluids to produce slurries, for example, water, vegetable oil and nitrogen gas (Cook 2009). The slurry is intended to be pumpable, which allows injection; and also has a known behaviour in groundwater. It may be that the desired behaviour is for the iron NPs to disperse through the aquifer carried by groundwater flow, or the opposite, so that iron NPs remain close to the injection points, depending on the desired remediation application.

Typically, iron NP injection can be carried out using several methods (Müller and Nowack 2010, US EPA 2008):

- Direct push techniques involve a direct push rig or stationary injection point to introduce iron NP slurry into the treatment zone.
- Pneumatic or hydraulic fracturing uses air or water to create a fracture network of preferential flow paths around the injection point and enhance iron NP distribution.
- Pressure pulse technology uses regular pulses of pressure while injecting the iron NP slurry.
- Liquid atomization injection combines an iron NP-fluid mixture with a carrier gas (for example nitrogen) to create an aerosol that can be dispersed into the treatment zone.
- Injection via a gravity feed (Henn and Waddill 2006)

Recirculation may be used via upgradient injection wells and downgradient extraction wells to improve delivery of the particles. The abstracted groundwater is usually mixed with additional particles and re-injected in the injection wells (US EPA 2008a). In the case of the initial field demonstration of the nZVI technology, a recirculation loop was established using a piezometer couplet situated approximately 15 feet downgradient from the injection well. Groundwater was extracted using the deeper piezometer and was amended with relatively low concentrations of nZVI (approx. 1 g/L), passed through a flow meter and then re-injected into the injection well (Elliott and Zhang 2001). Because the natural hydraulic gradient at the site was quite flat, the flow recirculation loop was used to artificially enhance movement of the injected iron mass within the relatively small test area (Elliott and Zhang 2001).

The choice of method and detailed design of the injection process (e.g. injection point spacings) is site specific. It depends on the amount (concentration and flux), disposition of contamination within the groundwater; the nature of the aquifer materials and how

these affect sorption / desorption of both contaminants and iron NPs; the hydrogeology of the site (including stratigraphy, permeability, groundwater flow etc); the type of iron NPs to be used (considering their reactivity, half-life and mobility in the subsurface, their materials handling properties and the estimated system redox demand over time) and the existing natural attenuation capacity of the aquifer (taking into account likely contaminant removals by biodegradation given the available electron acceptors).

These considerations affect the choice of iron NP to be used and the design of the injection approach, for example: spacing of injection points, depth of injection, amounts to be injected at each point, and the frequency of injections over time. From a pragmatic point of view the range of design choices is not endlessly variable. Often only one or two iron NP products will be available or offered by the service provider, so the injection approach will be designed around the offered product.

2.3.1.2 Iron NP Applications in Permeable Reactive Barriers

A permeable reactive barrier (PRB) relies on ensuring contaminated groundwater flows through a closely controlled treatment zone (see Figure 4). Hence a PRB typically treats dissolved phase contaminants. The treatment zone can be considered conceptually in three parts: an active agent, a matrix that supports and anchors the agent which is permeable to groundwater flow; and some form of containment for this matrix. There are many possible PRB configurations (Environment Agency 2002, Parbs and Birke 2005). These range from highly engineered approaches like the Funnel and Gate™, where sheet piling directs groundwater flow in a funnel to an engineered treatment gate which contains the matrix and its active agents; to barriers where an active agent is simply injected *in situ* in a form that does not migrate, in a location where groundwater flow naturally tends to concentrate, see Figure 7. In this latter case the aquifer materials form the containment and the matrix. Cundy *et al.* (2008) describe test work where iron [permeable] barriers are placed *in situ* using electric fields generated from iron rich electrodes, although this has yet to deliberately exploit nano scale processes.

The relatively short functional life times of iron NPs in the environment would appear to militate against them being used in PRBs, whereas conventional ZVI has been widely used in PRBs. However, their use in PRBs has been proposed several times (e.g. Kanel *et al.* 2007). Olsen and Lee (2006) proposed the use of nano-scale iron (II) sulphide in PRBs. However, it has been postulated that iron BNPs stabilised in some kind of a matrix might have improved longevity, which is essentially a PRB configuration. Furthermore, the matrix might render them more recoverable, and so facilitate the recycling of the precious metals used to dope the iron NPs (Yan *et al.* 2010).

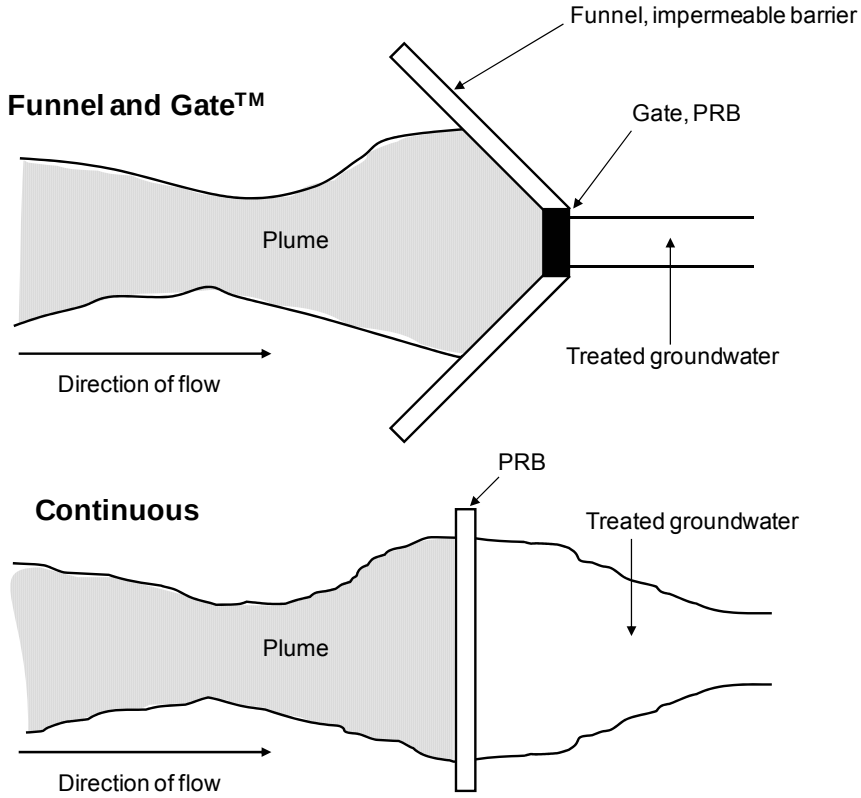

Figure 7 Funnel and Gate™ and Continuous PRB Configurations (from Nathanail *et al.* 2007*)*

2.3.2 Source Management Applications of Iron NPs via Direct Injection

The only practical means of delivering iron NPs for source management *in situ* is via direct injection. For a source management application the iron NPs need to be delivered in the vicinity of the solid phase or NAPL phase from which the groundwater (or vapour phase) plume is originating. Figure 8 shows several features of injection to deal with a DNAPL source: the bulk of the DNAPL sits beneath the groundwater on the aquifer's confining layer (as it is denser than water), and may exist in multiple pools, separated across all three dimensions by discontinuities in the subsurface (Environment Agency 2003). The iron NP injection needs to be engineered so that iron NPs are delivered to each of the separate individual sources, and this will require a detailed knowledge of the subsurface and the disposition of DNAPL within it.

ZVI has also been used as a "polishing" step where the source has been removed by excavation. In this application it is included with the backfill materials to treat impacted water as it passes through the higher permeability back-fill material.

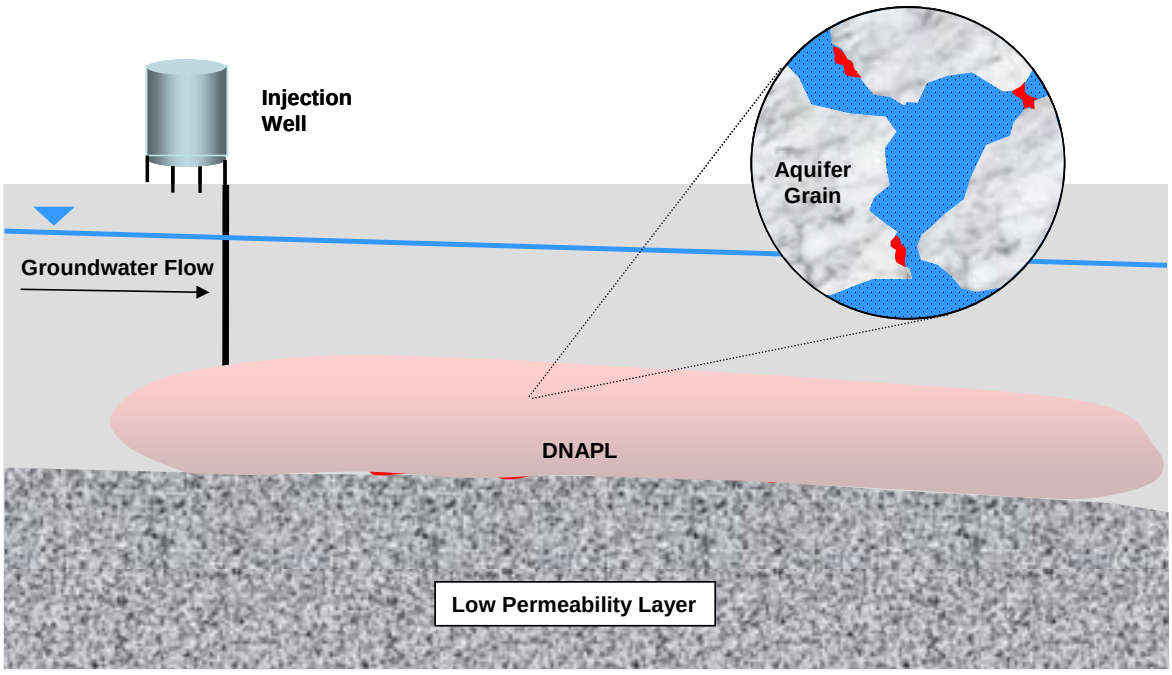

Figure 8 Injection of iron NPs into a DNAPL Source Zone (the red colour denotes the presence of NAPL in the subsurface). Adapted from Tratnyek and Johnson (2006)

2.3.3 Performance of Iron NPs in at the Field Scale

58 iron NP field studies have been identified (see Annex 2). As is often the case with field demonstrations it is difficult to find directly comparable information/parameters with regards to performance and effectiveness of treatment. The reasons for this are varied but include:

- Reporting before the projects or their monitoring is concluded;
- Complex, qualitative remedial targets (e.g. Several contaminants, different hotspots or compliance points);
- Different ways of reporting efficacy (e.g. % mass removal, concentration differences from different points); and
- Reluctance to report performance for commercial or operational reasons.

Consequently only general conclusions can be drawn with any confidence. Claims made are also subject to some controversy. Müller and Nowack (2010) see a number of benefits for iron NP compared with conventional ZVI. However, certain remediation vendors, such as Adventus, have disputed these claims (Adventus 2010). Adventus questions the validity of claims made for iron NP treatment costs and cost effectiveness, and also suggest that in practice transport of iron NPs is usually limited to a few metres at most from the injection point.

The majority of case studies listed in Annex 2 attempted both mitigation of source zones and management of pathways simultaneously, or did not differentiate between them. 88% of these examples are concerned with the remediation of chlorinated ethenes (chlorinated solvents), and this application can therefore be considered fairly well demonstrated in the field. Reported case studies are documented in Müller and Nowack (2010); Wei *et al.* (2010); Comba *et al.* (2011); U.S. EPA (2008a); U.S. EPA (2008b); Pupez *et al.* (2007); Li

et al. (2006); Gavaskar *et al.* (2005); Quinn *et al.* (2005); Gheorghiu *et al.* (2004); Glazier *et al.* (2003), Elliott and Zhang (2001); and Henn and Waddill (2006). The remainder of the other field trials primarily looked at the remediation of pesticides, Cr (VI), PCBs and Trichloroethane (TCA). PCB treatment is recorded in field-scale treatments in: Mikszewski 2004; Mueller *et al.* 2010; and U.S. EPA 2008. Cr(VI) field-scale trials are reported in: Müller and Nowack (2010); and Kvapil (2010).

While reductions in contaminant mass were reported, the major limitations of iron NP use for source management appear to be stoichiometric and mass transfer-related considerations. Multiple iron NP injections will almost certainly be required to effectively treat typical source areas. Since the nZVI reduction of amenable contaminants is a surface-mediated process, the lack of effective mixing in the subsurface could limit effectiveness.

It appears that the iron NPs prove very effective around the time of injection, nevertheless it is noted that not enough studies have been able to observe for long-terms effects of the injections. The case studies suggest that there is still work to do in order to prove long term remediation efficacy and avoidance of contaminant rebound in groundwater. The abiotic reduction reactions of chlorinated solvents in contact with iron NPs should produce very low levels of lesser chlorinated intermediate products. Nevertheless, chlorinated intermediate products are still observable when applying iron NPs to chlorinated solvents at field-scale. These may have a biological origin (see Section 3.2) but often field scale data is not adequate to demonstrate whether or not this is true.

Comba *et al.* (2011) carried out a meta-study across a number of field scale projects, and attempted to analyse these on a statistical basis. They concluded that the performance of nano-scale iron is poorer than larger particle sizes of ZVI for managing chlorinated solvent problems in groundwater, and that catalyst addition does not significantly improve performance under field conditions. However, their findings are open to considerable interpretation and doubt because of weaknesses in their approach. In particular, their dataset is not sufficiently defined with respect to key site-specific factors like the treatment methodology, timeframes, and analysis of post-injection results to make meaningful comparisons between treatment efficiencies. These perspectives, coupled with a relative lack of iron NP field studies that have tracked efficacy over substantial timeframes (i.e. 1-2 years or greater) or which have reached regulatory clean-up targets, understandably give rise to reservations about the technology.

Gavaskar *et al.* (2005) report on practical trials of iron NPs and conventional ZVI for source remediation. They used bimetallic nanoparticles, consisting of 99.9% iron and 0.1% palladium and polymer support, by mass. This was tested at two sites contaminated with chlorinated aliphatics (TCE). In each case approximately 136 kg of iron NPs were injected by direct push (assisted at one site by closed loop recirculation of groundwater). At one site a decrease in groundwater oxygen reduction potential (ORP) to – 200 mV was detected along with a partial degradation with an increase in concentration of *cis*-DCE. At the other site no change in ORP was detected and chlorinated aliphatic concentrations in the groundwater changed only gradually. In this latter case a more dilute iron NP slurry had been used. Gavaskar *et al.* (2005) concluded that the dosage of iron NPs needed to be large enough to create a more reducing environment far more quickly, and that enough mass of iron NPs needed to be injected to maintain this reducing environment over time. A much larger mass of conventional ZVI was injected at a third site which led to a substantial drop in ORP and increase in groundwater pH. This was associated with a reduction of chlorinated aliphatics without build-up of process intermediates. A second injection of ZVI elsewhere on this third site, but at a lower dosage, was also associated with a smaller reduction in ORP and persistence of DCE and VC.

2.3.4 Emerging Approaches

Integrated technologies have been researched for ZVI PRBs over the past decade, combining iron with heating (Fatemi *et al.* 2008), electrokinesis (EK) (Weng *et al.* 2007), microbial degradation (Van Nooten *et al.* 2008), or applying methods to reactivate the iron. The integration of iron with EK is also being explored to enhance the performance of iron NPs. Yang *et al.* (2008) used a laboratory column experiment to assess the ability of EK coupled with injection of a Fe/Pd BNP slurry to treat nitrate-contaminated soil. A transport distance of 9 metres was calculated, based on the sticking coefficient, and nitrate removal of over 99% was achieved with only 0.05%wt. BNP injected. Shariatmadari *et al.* (2009) used a bench-scale test to assess the efficacy of coupled electrokinetic migration and a nZVI reactive wall in reducing Cr(VI) in clayey soil. Reduction and removal efficiencies of 88% and 19% were achieved, with removal increasing to 42% by maintaining the pH at a constant 6.3 near the anode. No field studies have taken place, but the early research is promising. Pamukcu *et al.* (2008) report that at laboratory scale applied electric fields may also enhance iron NP activity.

The use of iron NPs has also been found to be compatible with (and indeed to potentially enhance) biological processes of dehalorespiration (see Section 3.2)

The University of Greenwich has been investigating the potential of iron NPs to stabilise DNAPL emulsions in the subsurface. Their concept is a source term treatment where the iron NPs create an emulsion of DNAPLs which can then be removed by groundwater pumping, with residual iron NPs acting to degrade any remaining DNAPL (Leharne pers. comm.).

Iron oxide has been tested as a sorbent for removal of arsenic from groundwater (Cundy *et al.* 2008). Iron oxide nanoparticles have been considered for removing arsenic from groundwater. Laboratory scale tests have shown that they bind to arsenic and can then be removed from the water magnetically (Rickerby and Morrison 2007). Cundy *et al.* (2008) point out the possibility of using immobilised iron NPs as filter for contaminated groundwater in a PRB, or in an *ex situ* filtration system.

3 BENEFITS OF USING IRON NPs IN REMEDIATION

In the UK, and indeed worldwide, the majority of remediation work is based on excavation and removal or containment, although the role of landfill is slowly diminishing. Process based technologies (exploiting biological, chemical, physical solidification / stabilisation and thermal) technologies are employed, but still only on a minority of projects. Process based technologies have their greatest market penetration for problems where excavation and removal is not feasible and an *in situ* solution is necessary, in particular for treatment of contaminated aquifers.

Some proponents of the use of iron NPs see it as a remediation intervention capable of delivering a substantial improvement in remediation performance for a wide range of problems. This view is based at least in part on projections from laboratory-scale performance (Müller and Nowack 2010, Rickerby and Morrison 2007, Tratnyek and Johnson 2006). However, like many remediation techniques, the transfer of use of iron NPs from laboratory scale experiments to practical remediation applications has seen this potential constrained.

The broad benefits seen for using iron NPs fall into a number of categories: extending the treatable range of contaminants and improving the effectiveness of contaminant destruction; improved remediation efficiency, providing source term treatment capability; improved ease of use compared with other forms of ZVI; longevity of action; cost effectiveness and wider application benefits. Each of these categories is described in more detail in the sections following.

3.1 Extending the Treatable Range of Contaminants and Increasing Treatment Speed

Iron NPs are able to deliver a very high specific surface area for chemical reactions per unit mass of iron added. Owing to their smaller particle size and hence greater surface area per unit volume, iron NPs can increase reaction rates and potentially allow greater penetration through the subsurface in comparison to micro-scale or granular ZVI equivalents. In addition, the nano-scale effects may allow different chemical processes extending the range of treatable contaminants (for example catalytic effects), although the treatment route remains redox leading to the destruction of organic contaminants and the transformation and/or precipitation of inorganic contaminants (Liu *et al.* 2005, Song and Carraway 2005, US EPA 2008, Zhang 2003). The use of iron NPs is therefore seen as allowing a more effective dosage of a treatment area with iron, because a greater amount of iron is more readily available for reaction with contaminants compared with microscale ZVI (e.g. Li *et al.* 2008).

Iron NPs may also have advantages over ZVI for *in situ* stabilisation (and reduction) for a range of potentially toxic elements (Li *et al.* 2006a and 2006b) and have also been considered as a treatment for radionuclides such as radium and uranium (Burghardt and Kassahun 2005). Iron oxide NPs, and nano-scale iron (II) sulphide have also been tested at laboratory-scale for removal of arsenic (and other anionic trace elements) for remediation (Han 2009; Ramos *et al.* 2009; Shipley *et al.* 2010). Nano-scale iron phosphate has been tested at laboratory-scale for the immobilisation of copper (II) and lead (Liu and Zhao 2007a and 2007b). Nano-scale / 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). Iron NPs can also be used to reduce nitrate (Park *et al.* 2008) for example in a PRB (Bezbaruah *et al.* 2009a), although presumably this would not be cost effective for most nitrate contamination of groundwater

problems. However, the consequence of this is that nitrate in groundwater may passivate iron NPs and so both reduce their effectiveness and increase their persistence, see Section 3.6.

Iron NPs have also been doped with other metals which improves their reactivity and the range of treatable problems by introducing extended catalytic properties (Cook 2009, Sirk *et al.* 2007, Saleh *et al.* 2007, see Section 2.2.2).

Laboratory studies (e.g. Lowry and Johnson 2004) using iron NPs have demonstrated a broader range of treatment capability for contaminants compared with both conventional ZVI and biodegradation; including treatment of polycyclic aromatic hydrocarbons (PAHs), complex chlorinated aromatic compounds (such as PCBs), pentachlorophenol (PCPs), and the chlorinated benzenes). Table 5 compares the known treatability of contaminant categories by iron NPs, conventional ZVI and biodegradation based on bench scale work, and field scale observations. However, this extended range of treatable contaminants is not as well documented in the field. Field scale test-work and practical applications of iron NPs have focussed on chlorinated solvent problems (see Section 2.3.3).

Table 5 Comparison of Contaminant Laboratory Scale Treatability for Iron NPs, Conventional ZVI and Biodegradation

Contaminant	Iron NPs	Conventional ZVI	Biodegradation
Chlorinated Solvents (i.e. Tetrachloroethene (PCE); Trichloroethene (TCE); Cis- / Trans- / 1,1-Dichloroethene (DCE); Vinyl chloride (VC); 1,1,1-trichloroethane; 1,2,3-trichloropropane. C3 and C4 compounds. Chlorinated methanes.	- Elliott *et al*. 2008 (hexachlorocyclohexanes); Lien and Zhang 1999 (Chlorinated ethanes);	- mZVI can also be used to remediate chlorinated solvents. Literature suggests the lower reactivity results in less agglomeration, farther aquifer migration (both w.r.t. non-stabilised/coated nano-iron) albeit with lower efficacy.	- Bioremediation using biodegradation is widely practiced for degradation of chlorinated aliphatic solvents, and has been successfully implemented on hundreds of sites worldwide. The bioremediation approach taken uses the anaerobic process of dehalorespiration, following injection by a wide range of products including molasses, vegetable oil and Hydrogen Release Compound (HRC®). In some cases intermediate products are found to accumulate (DCE and VC), although there are several additional measures that could be used to deal with this problem including biostimulation and bioaugmentation. Alternatively a second stage aerobic process can remove VC. Bioremediation for chlorinated solvents is primarily a pathway management technique and is less effective for source zones where free NAPL is present. - There is also good evidence supporting dehalorespiration for treatment of substituted methane compounds. - Field based evidence for treatment of brominated aliphatics and C3 / C4 aliphatics is less well established, although more work on chlorinated aliphatics has been published.
Chlorinated Aromatics (Hexachlorobenzene; Pentachlorobenzene; Tetrachlorobenzene; Trichlorobenzene; Dichlorobenzene;	- Laboratory based studies evidenced in: Lee *et al.* 2010; Shih *et al.* 2009; Cheng *et al.* 2007 (p-chlorophenol); Cheng *et al.* 2010 (pentachlorophenol and chlorophenols); Zhu & Lim	- Cheng *et al*. 2007 (p-chlorophenol);	

Contaminant	Iron NPs	Conventional ZVI	Biodegradation
Chlorobenzene)	2007 (chlorobenzenes), Zhu *et al.* 2008 (trichlorobenzene)		
Pyrene	- Chang *et al.* 2007; and Chang and Kang (2009) indicated through batch experiments that nZVI particles were more efficient in removing pyrene than commercially available microscale ZVI.		
PCBs	- Considerable laboratory-scale work evidence suggests that PCBs can be treated effectively, with a limited number of papers demonstrating this at field scale. - E.g. Lowry and Johnstone 2004; Choi *et al.* 2008,	- Mikszewski (2004); reviewed the evidence, suggesting mZVI shows limited promise in remediation of PCBs at field scale.	- Limited land based evidence of PCB and dioxin biodegradation, but these compounds are not usually regarded as biologically treatable using current technologies. Nevertheless empirical data in Mikszewski (2004) states that in general, microbial reductive dechlorination of PCBs removes *meta* and *para* chlorines from highly chlorinated congeners, resulting in predominately *ortho* substituted mono- through tetrachlorobiphenyls (Wiegel and Wu 2000).
Dioxins	- Laboratory studies show promising polychlorination of dibenzo-*p*-dioxins and furans (PCDD/Fs) using palladized nanosized ZVI (Kim *et al.* 2008); 2,4-dichlorophenol dechlorination by Pd-Fe bimetallic nanoparticles (Zhang *et al.* 2008)	- Laboratory studies show polychlorination of dibenzo-*p*-dioxins and furans (PCDD/Fs) using palladized micro-sized ZVI (Kim *et al.* 2008).	
Energetic Compounds RDX (Hexahydro-1,3,5-trinitroperhydro-1,3,5-triazine)	- Laboratory studies showed the degradation of RDX by nZVI in the presence carboxymethyl cellulose (CMC) stabilizer (Naja *et al.* 2008).	- Laboratory studies (batch and column) showed that RDX can be degraded by granular iron and nickel-plated granular iron (Gui *et al.* 2009).	

Contaminant	Iron NPs	Conventional ZVI	Biodegradation
Inorganic cations (Mercury; Nickel; Cadmium; Copper; Lead; Silver)	- Literature search showed evidence of lead and cadmium stabilization / immobilisation proven at laboratory-scale only - Zhang *et al.* 2010 (Cadmium & Lead);		- Laboratory-scale and field scale demonstration projects have investigated heavy metal mobilisation /immobilisation using biologically produced sulphide ions. - Proprietary products that combine biological sulphide generation and metal immobilisation are marketed as remediation technologies
Inorganic anions (Arsenate/arsenite; Chromate/dichromate; Perchlorate)	- Cr(VI), As (III) & (V) and perchlorate removal by nZVI frequently evidenced at laboratory-scale. - Elliott *et al.* 2007 (perchlorate) and Cao *et al.* 2005 (CrVI).	- mZVI can also be used to reduce Cr(VI) albeit this study discovered literature evidence of this at laboratory-scale.	- Biological reduction of dichromate is regularly used as a remediation technique
Pesticides (DDT; Lindane, atrazine, alachlor)	- Numerous Lindane degradation studies at laboratory-scale only. Also DDT, alachlor and atrazine remediation has been trialled at laboratory-scale, e.g. - Bezbaruah *et al.* 2009b; Satapanajaru *et al.* 2008.	- Elliot *et al.* 2009 suggests from laboratory studies more favourable degradation rates using nZVI than the mZVI comparator.	- Many pesticide compounds are amenable to biodegradation, whereas others are recalcitrant. This can be isomer specific.
Brominated aliphatics (Bromoform; Dibromochloromethane; Dichlorobromomethane)	- Lim *et al.* 2007 (Brominated methanes);	- Lim *et al.* 2007 (Brominated methanes);	- Field based evidence for treatment of brominated aliphatics and C3 / C4 aliphatics is less well established, without any field evidence.

3.2 Extent of Contaminant Destruction

A claim made for the use of iron NPs in remediation is that they offer a complete treatment without the generation of toxic intermediate breakdown products, or generate more benign reaction products (Bezbaruah 2009b, Nurmi *et al.* 2005). Whilst the certainty of the claim is questionable due to the heterogeneous nature of *in situ* conditions, the statement is theoretically correct and one which could be realised in idealized conditions. Avoidance of toxic intermediates could be a major process benefit, particularly for sites where the pathway to potential receptors is relatively short.

The current practical trend in the use of iron NPs is for degrading chlorinated solvents such as percholoroethene (PCE). Bench scale studies of iron NP use (e.g. Henn and Waddill 2006) indicate that in their presence PCE is degraded fully to ethane. This has been compared with the field scale performance of *in situ* bioremediation for treating chlorinated solvents, where there are instances of the accumulation of toxic intermediate products dichloroethene (DCE) and or vinyl chloride (ITRC 2008). However, this claim must be treated with care.

- Firstly, *in situ* bioremediation in practice can proceed to closure without stalling at the DCE and VC stages. The reasons for DCE accumulation are typically site specific. There is a body of evidence which suggests that it is because the local microbial community lacks a DCE degrader. This has been successfully remedied in a number of cases by inoculation of the aquifer with *Dehalococcoides* (ITRC 2008).
- Secondly, there are reports of intermediate product accumulation during iron NP treatment of chlorinated solvents.

Available evidence therefore supports a view that process intermediates may accumulate for both *in situ* biodegradation treatments and iron NP applications in the field, depending on site specific circumstances (and the sufficiency of added iron NPs). However, it is also possible that the process intermediates observed during iron NP use in the field may be a consequence of biological processes rather than abiotic processes.

3.3 Efficiency of Treatment

Two important factors associated with the potential application of iron NPs in an environmental remediation context include their cost relative to field benefits achieved and their quality assurance/quality control (QA/QC) profile. With respect to the former, laboratory studies suggest that for a given contaminant, iron NPs are more reactive than conventional ZVI, and therefore may be a more effective remediation agent (See Section 3.1). However, the reactivity of the iron only represents part of the overall cost-effectiveness. The cost of the iron is obviously a key consideration and, at present, iron NPs costs are typically on the order of $30-40/lb while conventional ZVI is on the order of $1-5/lb and granular iron is generally in the range of $0.25-0.75/lb (D.W. Elliott, 2011 Pers Comm). Based on laboratory investigations, smaller amounts of the more reactive (and expensive) iron NPs would theoretically be needed but it is difficult to quantify the magnitude. Similarly, the more reactive iron NPs can reasonably be expected to exhibit a faster utilization rate in the field which could mean that multiple injections of iron NPs may be required. All of these considerations are quite site-specific and besides the type of iron being considered, will depend on factors such as the local hydrogeology and suite of contaminants to be treated. Therefore, while it is challenging to predict the overall efficiency of treatment due to the many variables in play and to their site-specific nature, it can be generalized that iron NP technology is better capable of degrading the more recalcitrant environmental contaminants (e.g. chlorinated aromatics, chlorinated pesticides, etc.).

QA/QC for iron NPs is an important consideration because of the diverse array of manufacturing methods and suppliers. This stems from the fact that iron NPs are fundamentally reactive species with properties that are not static but change over time. Because of this, nZVI that was manufactured months in advance of field use may experience a significant loss of reactivity. While no specific metrics exist in this regard, the best practice is to use the nZVI as soon after manufacture as practical given its inherent reactivity. Other potential concerns could include the presence of toxic metals or other trace constituents in the source material for the iron NPs. Insofar as material QA/QC is concerned, practitioners should be knowledgeable of the intrinsic properties/characteristics of the iron being used in the remediation project. Key QA/QC parameters include particle size distribution (PSD), specific surface area (SSA), pH/ORP profile, and reactivity against a standard contaminant (e.g. 1 mg/L aqueous solution of TCE).

3.4 Source Management Applications

The high reactivity of iron NPs has led to suggestions that it could be injected as an *in situ* source management application, capable of rapidly destroying NAPL (Geiger *et al.* 2002, Quinn *et al.* 2005). In practice, the ability of iron NPs to reduce the amount of contamination as a source is limited by the accessibility and availability of the source contamination (= "source term") to the iron NPs being supplied to treat it, and the physical amount of iron that is needed to oxidise the source term.

Generally iron NPs are highly reactive to contaminants in the dissolved phase and the sorbed phase, and technologies to enhance activity against the free phase have also been tested such as eZVI (reviewed in Chapter 2). However, at a field scale it is the delivery of the treatment agent to the contamination problem that fundamentally constrains remediation performance, i.e. the accessibility of the contamination to be treated. This accessibility is constrained by the permeability of the subsurface, subsurface heterogeneities and their potential to limit flow and/or create preferential pathways of flow and discontinuities such as the phase difference between the groundwater and the NAPL.

This is a general limitation for *in situ* source term treatments for groundwater problems which typically have a limited effectiveness. Complete mass removal is rarely possible, and because only low concentrations of sparingly soluble NAPLs can exceed threshold values, the residual source term is still problematic (Gavaskar *et al.* 2005, Teutsch *et al.* 2001).

Nonetheless while there is great interest in iron NPs as a source zone treatment for chlorinated solvents, *in situ* anaerobic bioremediation of DNAPL source areas has received considerable research attention in recent years (ITRC 2008).

3.5 Ease of Use

Treatment agents may be delivered *in situ* by injection using pumping via wells (flushing), direct push; or via engineered installation such as PRBs. The ease of use benefits of iron NPs are largely argued on the basis of improved delivery to the subsurface compared with conventional ZVI, and an improved ability for it to migrate through the subsurface, again compared with conventional ZVI as it is able to remain in suspension, particularly in amended or stabilised forms (see Section 2.2). However, there is a trade-off between reactivity and mobility in the subsurface, so the more mobile formulations tend to be less reactive (see Section 4.4.2)

In practice improved injectability, materials handling and migration from injection points have proved hard to deliver in some projects. The injection of iron NPs has proved to be difficult for some operators and mobility of the iron NPs has often been limited to several metres from injection points (Uyttebroek *et al.* 2010). Furthermore, iron NPs are highly reactive; indeed if present as dry solids, they are spontaneously combustible in air, and also need to be handled as potentially hazardous to human health. Typical applications in environmental remediation involve the iron being transported and utilized in the field as a slurry, or in a nitrogen atmosphere in sealed containers (Müller and Nowack 2010). Great care must be taken in handling and use to avoid inactivation of the iron NPs before they reach their target as they will readily sorb to and react with surfaces (Baer *et al.* 2007).

The most critical elements to field successes with nZVI are the development of a robust site conceptual model based on well-characterized site conditions (e.g. contaminant distribution, geochemistry, and hydrogeology) and sufficiently permeable hydrogeologic conditions (e.g. hydraulic conductivity of 10^{-4} cm/s or higher). With respect to the deployment of nZVI, it is important for the field crew to be experienced with *in situ* remediation generally and with specific amendment delivery using standard push direct injection and the use of well infrastructure. Clearly, it would be advantageous for the field crew and consultants to be familiar with the nZVI technology and have a demonstrated track record in the field.

3.6 Longevity of Action

Even stabilised iron NPs have limited persistence in the environment, on the order of months at most (see Section 4.4.3). While this militates against their use in PRBs, it is perhaps useful for some remediation interventions that the treatment agent does not persist or where limited mobility is desired (i.e. source area treatment). In general, the types of surface modifiers that have received most of the research attention are relatively biodegradable. Therefore, it is reasonable to assume that these surface architectures will be subject to degradation which, in turn, would affect iron NP stability and mobility in the subsurface.

Laboratory studies indicate that the fate of iron NPs is ultimately to be converted into larger particles of iron (II) and (III) oxides (Reinsch *et al.* 2010, Sohn *et al.* 2006). The rate of oxidation may be inhibited by anions commonly encountered in groundwater, in particular nitrate (Reinsch *et al.* 2010). This passivation effect has also been found to be inhibitory to iron NP treatment of TCE (Liu *et al.* 2007).

It is possible that iron NPs which have been sorbed or which have agglomerated may yet release active iron NPs at some point in the future. Moreover, the surface architectures of modified iron NPs could serve as potential carbon sources or stimulate anaerobic biodegradation processes in the environment. However, there appears to be little in the way of measurements in the technical literature to support or disprove these assertions.

3.7 Cost Effectiveness

Iron NPs do tend to be expensive compared to their larger scale counterparts, on a per unit basis (as in Section 3.3), although economies of scale in production may yet have an impact on costs. Nevertheless, nZVI is more reactive than other iron forms. Well delineated contaminant plumes in moderately to highly permeable (i.e. $K > 10^{-5}$ m/s) hydrogeological formations are likely to represent the fundamental conditions under which iron NPs are best suited for use. However there is very little information in the peer-reviewed literature with respect to cost analyses for iron NP remediation projects. Due to this paucity of information, and the possibility that iron NP effectiveness may be very site-

specific, it is very difficult to extrapolate field-scale remediation costs from bench-scale testing data. However, anecdotal data suggest that that the cost of the iron NPs is likely not the driver for the overall remediation cost. The overall remediation cost depends more on the extent of infrastructure (i.e. wells, pumps, recirculation loops, etc.) needed to deliver the iron NPs and the number of rounds of treatment required (D.W. Elliott 2010 Pers. Comm.). Other significant components in the cost equation include the required analytical testing, consultant/contractor labour, and reporting. Costs are even harder to estimate for more recalcitrant contaminants like the chlorinated benzenes. All other factors notwithstanding, cost effectiveness of the iron NP approaches will decline in low permeability formations as well in areas that are poorly characterised in terms of the nature and extent of contamination. However, such a decline in cost effectiveness in the absence of good site specific information is probably a common feature of most remediation approaches.

Cost effectiveness appears to be highly dependent on a site's specific circumstances. In some circumstances iron NPs may be more cost effective than conventional ZVI, and in others *vice versa* (Cook 2009).

3.8 Compatibility with Other Treatments

Interestingly field and laboratory scale observations indicate that iron NP use is synergistic and stimulatory for *in situ* biodegradation of chlorinated solvents by dehalorespiration. Laboratory studies indicate that application of iron NPs does not appear to be inhibitory to (and may even be stimulatory for) biological reductive dechlorination associated with water-derived cathodic H_2 production during its anaerobic corrosion (Kirschling *et al.* 2010, Xiu *et al.* 2010), and also where the iron NPs have biodegradable coatings. These laboratory findings are consistent with observations during applications of iron NPs in the field, where biological reductive dechlorination continues or is stimulated (e.g. He *et al.* 2010). However, Barnes *et al.* (2010) report on UK microcosm experiments which indicate that nano-scale iron-nickel particles are inhibitory to biological dechlorination, which is contrary to the findings generally reported for iron NPs.

3.9 Sustainability Considerations

Ensuring that remediation not only serves a risk management function, but is also sustainable is now a major theme of development internationally (Bardos *et al.* 2011). Within the UK CL:AIRE has organised the Sustainable Remediation Forum – UK (SuRF-UK) which has published a framework on ensuring sustainable remediation (SuRF-UK 2010). CL:AIRE has also carried out a general review for Defra of the sustainability of the principal remediation approaches (Defra 2010), although this did not include use of iron NPs as this is not a current approach within the UK. Sustainability encompasses a range of considerations and the balance of benefits and impacts is typically dependent on the specific context of a contaminated site, rather than being attributable to different technology types in general. Potential sustainability assets for nano-remediation might be its ability to effect a complete destruction of some contaminants without leaving intermediate breakdown products, and also extending the range of contaminants that can be dealt with by destruction rather than extraction or stabilisation. Concerns tend to relate to the use of resources and energy for their manufacture, particularly use of rare metals for doping as well as general societal reluctance to adopt new technologies. The balance of benefit over impact will be highly dependent on the context of the project, with no known sustainability appraisals of iron NP applications for remediation in practice made to date.

3.10 General Appraisal of Benefits

Overall iron NPs do not offer a step change in remediation technology performance in a generic way. However, for chlorinated solvent problems iron NPs may be a highly effective solution. They appear to be cost effective in several pathway management applications in a number of countries, and eZVI formulations may offer a novel source management technique for non-aqueous phase liquid (NAPL) contamination problems.

The potential advantages of using iron NPs based on projections from laboratory-scale test-work exceed those that have been demonstrated in the field. This is principally due to the heterogeneous nature of ambient conditions effecting perfect dispersion, contact and reactions, but also due to insufficient field demonstrations which have a significant open learning legacy. The gap between field potential and field demonstration is exemplified by the field potential of iron NPs in treating contaminating anions and cations (such as arsenic and chromium) which is not yet sufficiently proven through field demonstrations. There is some evidence to suggest that they may extend the range of treatable contaminants with reduced risks of toxic intermediate compound production. In addition, in some cases it is possible for the technology to avoid taint of groundwater, which may be a consideration in some applications close to surface water receptors. Major research, development and demonstration investment continues to take place so improvements in the use of nano-iron as a remediation approach should be expected.

The vast majority of published field studies relate to the destruction of chlorinated solvents. Chlorinated solvents, such as the chloroethenes, are recalcitrant problem contaminants, where destructive treatment will frequently be the most desirable management option. Treatment efficacy is a key consideration as practitioners work to degrade the contaminants in the most cost-effective manner. Chlorinated solvent sites are so prevalent that a viable market for the technology has arguably already been established and has “driven” field-scale research.

It seems likely in the UK at least, that iron NPs role will be as a niche technology in the near to medium term. Service providers who have an established track record of successful iron NP applications in other countries will be best able to provide solutions acceptable to regulators, and offer solutions with the smallest project risks. This will offer them a major competitive advantage.

4 RISKS ASSOCIATED WITH USING IRON NANOPARTICLES FOR REMEDIATION

The 2004 report from The Royal Society/ Royal Academy of Engineering (RS/RAE) played a large part in setting the agenda for nanotechnology in the UK. In the context of this report, two of the RS/RAE's recommendations are particularly relevant:

- **RS/RAE Recommendation 4** Until more is known about environmental impacts of nanoparticles and nanotubes, we recommend that the release of manufactured nanoparticles and nanotubes into the environment be avoided as far as possible
- **RS/RAE Recommendation 5** The use of free (that is, not fixed in a matrix) manufactured nanoparticles in environmental applications such as remediation be prohibited until appropriate research has been undertaken and it can be demonstrated that the potential benefits outweigh the potential risks

The Government response to RS/RAE report heeded the warnings of uncertainties associated with nanoparticle behaviour, toxicity and fate in the environment:

- **Recommendation 4** We support this recommendation and will work with the Environment Agency and other stakeholders (including Local Authorities), in partnership with industry, to identify and help reduce or remove any waste stream discharges containing manufactured nanoparticles and nanotubes and prevent nanoremediation using these from taking place until we have a fuller understanding of the risks.
- **Recommendation 5** In order to further our knowledge of the environmental fate of nanoparticles and nanotubes and their potential for environmental remediation, some small-scale controlled environmental release may be needed. The Government will review legislation covering environmental release for research purposes within the regulatory review to ensure that any release is undertaken in a safe and controlled manner and does not pose significant risks to the environment and human health.

More recently the Government published the "UK Nanotechnologies Strategy" (HM Government 2010). It recognised the role of government in encouraging a "cohesive and flourishing industry" while "also acknowledging and addressing the implications for health, safety and the environment". The Government quoted a Technology Strategy Board prediction of phenomenal growth in environmental and water sector nanotechnologies revenues from 86M USD in 2007 to 3,885M USD by 2015. The need for public confidence in nanotechnology was highlighted and active engagement with the public was seen as essential in developing such confidence.

Additionally, Defra chairs the Nanotechnology Research Strategy Group (NRSG). The NRSG has established a series of 5 task forces:

- Task Force 1: Metrology, Characterisation, Standardisation and Reference Materials
- Task Force 2: Exposure – Sources, Pathways and Technologies
- Task Force 3: Human Health Hazard and Risk Assessment
- Task Force 4: Environmental Hazard and Risk Assessment
- Task Force 5: Social and Economic Dimensions of Nanotechnologies

Hence, the Government's position has been to advocate the responsible development of the technology through parallel assessment of both the risks and benefits. Both the

Government and Environment Agency have therefore been receptive to controlled trials taking place and have since been active in supporting relevant research through, for example, the Environmental Nanoscience Initiatives and the Environmental Exposures and Human Health programme.

4.1 Potential and Known Risks of Releasing Iron NPs into the Surface and Subsurface Environment

Iron NPs are used to destroy contaminants that are known to be persistent in the environment, recalcitrant to many treatments and highly toxic to human health. This is a perhaps unique context within which to consider the risks posed by iron NPs.

The ability of a substance to cause harm to a remote receptor is a function of:

a. Fate – will the substance survive in the environment

b. Transport – will the substance be able to reach the receptor

c. Toxicity – how will the substance harm the receptor

The use of conventional ZVI (for example in PRBs) has been to dechlorinate contaminants such as vinyl chloride, dichloroethene, trichlorothene and tetrachlorethene (Nathanail *et al.* 2007). The very low health criteria values of such contaminants render these contaminants among the most toxic to human health (Nathanail *et al.* 2009). In contrast, iron did not even feature on a list of some 60 substances identified by the former Soil Guideline Value (SGV) Taskforce as being a priority for the development of a SGV.

Karn *et al.* (2009), suggests that "*our knowledge of the potential environmental and health hazards posed by these nanomaterials is* [acknowledged to be] *in its infancy*". Acknowledging the relatively immature understanding it is perhaps surprising that commentators of various backgrounds have not used a lines of evidence approach to predict the likely coordinates of the mature position at which they would like us to arrive.

Du Pont (2007) raised doubts about both the quality and the relevance of vendor supplied environmental, health and safety (EHS) information: *"Toxicity, human hazard, and environmental fate and effects data available from potential suppliers are highly variable in both quality and completeness. In many cases, it is not clear from the information provided whether the EHS data is based on the nZVI or on larger sized simple iron powder."*

4.2 Risk Appraisal for Iron Nanoparticle Handling in Remediation

Once manufactured, the most significant health and safety risks for people working with iron NPs occurs during the transportation, handling, and injection of the nanoparticle slurries. Additionally, if 'top-down' synthesis of nanoparticles is employed then, depending on the manufacturing approach, there could be a higher risk posed to human health if dry nanomaterials are being processed. This is recognised in the literature, with Renn and Rocco (2006) stating "the higher surface reactivity and surface-area-to-volume ratio of nanopowders increases the risk of dust explosion and the ease of ignition". Such handling concerns are not unique to nanoparticles and the remediation sector has recognised the need for good handling, storage and transportation procedures for other hazardous substances, such as those used for *in situ* chemical oxidation. In fact, the potential safety considerations and liabilities associated with handling reactive iron powders represent a major hurdle for use in the field. Furthermore the practicalities of ensuring the safe handling of dry powders on site would mean it is extremely unlikely that any remediation

practitioner would consider using them. As far as we are aware, all field-scale remediation applications of iron NPs are as heterogeneous slurries, either in water or in an aqueous mixture with other materials (e.g. surfactants, alcohols, etc.).

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 nano-iron handling should follow procedures outlined in Material Safety Data Sheets (MSDS) or, in the UK, Control of Substances Hazardous to Health (COSHH) data sheets. The MSDS typically accompany the manufactured product and include the specific information relating to physical and chemical properties, identified hazards, acute and chronic health effects, first aid measures, fire fighting measures, accidental release measures, handling and storage, exposure controls and personal protection, transport, and regulation. Examples such as that provided by Quantumsphere (2007) show information on all of the above listed properties including toxicological data of the iron NPs. Practitioners should ensure that this information provided relates to iron NPs and not just the bulk form. In addition to the MSDS, practitioners must wear appropriate personal protective equipment (PPE) during slurry handling and injection. Recognition of potential hazards such as hydrogen gas evolution from aqueous iron NPs slurries in mixing tanks and direct-push injection equipment is important. As touched upon in Section 3.3, MSDS or QA/QC documentation with this type of information or level of detail are not commonplace in the emergent iron NP marketplace. Generally speaking, over the past several years, MSDS supplied with iron NP purchases tended to provide relatively generic data as very little toxicological, emergency response, and cleanup information was available. However, regulatory scrutiny and a recent research focus on the implications of nanotechnology use will likely change this trend.

4.3 Fate of Iron NPs in the Environment

4.3.1 Context of Natural Iron NPs within the Environment

Iron is a major component of many soil forming minerals. It is one of the most abundant elements in the earth. Nevertheless iron NPs represent new technology. This novelty coupled with some albeit inconclusive suggestions in the literature that small nano scale particles behave differently from their macro-scale counterparts requires a *de novo* examination of the fate and toxicity of iron NPs. The UK Government has taken the position that “methodologies to determine trace levels and the state of manufactured nanoparticles in complex media such as soils, sediments and waters are required.” (HM Government 2010).

Wiggington *et al.* (2007) note that "although synthetic nanoparticles are undoubtedly being released into the environment—and understanding the consequences of such releases are of major importance to environmental sustainability—they still only represent a minuscule fraction of the nanoparticulate matter in the environment at this time." Naturally occurring nanoparticles occur in the form of colloids including clay, oxides and organics (Degueldre *et al.* 2000). Gilbert *et al.* (2007) suggested that many manufactured metal oxide and other inorganic nanoparticles will exhibit cluster-forming behaviour similar to that of natural nanoparticles. Iron NPs within the aqueous environment are generally believed to transform to various iron oxyhydroxides, similar in composition to naturally-occurring iron oxide based minerals. Karn *et al.* (2009) suggest that this is why little concern has been raised about the widespread distribution of toxic effects stemming from iron NPs.

4.3.2 Key Characteristics

Many of the key characteristics determining the fate of iron NPs are related to their 'mobility' and 'reactivity'. Mobility and reactivity exhibit an overall inverse relationship so that nanoparticles with high reactivity often have low mobility because of their tendency to agglomerate and sorb to surfaces. Iron NPs modified for improved mobility (reviewed in Section 2) need to have somewhat lower reactivity in order to provide this mobility.

Zero-valent iron NPs, and especially those that are unmodified, are naturally attracted to one another, which can cause them to agglomerate into larger micron-sized particles (greater than 100 nm) (Tratnyek and Johnson 2006; Phenrat *et al.* 2007). Under laboratory conditions, these particles tend to agglomerate and produce potentially stable clusters that can build up to the micrometre size. If this occurs, they will adopt the behaviour of larger sized environmental colloids (Tratnyek and Johnson 2006), resulting in the loss of nano-specific characteristics. This agglomeration occurs very rapidly so that truly 'nano-scale' iron particles do not remain for a long time before creating larger 'nano-scale' and micro-scale iron, exhibiting behaviour more akin to that of micro-scale iron (D.W. Elliott 2010). Auffan *et al.* (2009) suggested that nano particles larger than 30 nm essentially behaved and should be regulated as their bulk counterparts, while nano particles smaller than 30 nm "*have a size-dependent crystallinity that gives them properties drastically different from the bulk material*". Even before agglomeration, most iron NP products are in the 60-100 nm size range, so following this suggested model of behaviour it would appear that for even the minority of particles smaller than 30 nm, the characteristics and behaviour of being nano-scale are short lived. However the Auffan *et al.* (2009) paper implicitly ignores specific surface area in the interpretation of particle behaviour and only uses a small data set (Lead pers comm.). Studies have shown that iron NPs may not achieve widespread distribution in the subsurface due to this agglomeration prior to complete dispersion within the soil or groundwater matrix, limiting the radius of influence. Agglomeration may also reduce the exposed reactive surface area of the particles.

Dissolved oxygen very rapidly oxidises iron NPs to various iron oxides. Any dissolved oxygen in groundwater will, therefore, use Fe^0 that would otherwise have been used for contaminant degradation (Reinsch *et al.* 2010). Iron NPs typically react within the subsurface to form nano-ironhydroxide or iron carbonate particles which have dramatically lessened reactivity due to the presence of the passivating oxide shell relative to the zero-valent core. Even with an inner-core of zero-valent iron these would be expected to essentially behave as iron hydroxides. Depending on general groundwater redox conditions being either oxic or anoxic, iron hydroxides or iron carbonates potentially form passivating layers on the nano-iron particle. Since the solubility of both of these minerals is considerable under acid conditions, the precipitation of these mineral phases is likely under the vast majority of natural aquifer conditions with a pH of greater than 7. Auffan *et al.* (2009) report that *"Analysis of published data suggests that chemically stable metallic nanoparticles have no significant cellular toxicity, whereas nanoparticles able to be oxidised, reduced or dissolved are cytotoxic and even genotoxic for cellular organisms*". Similarly, iron nanoparticle coatings can also mitigate the iron toxicity.

4.3.3 Reactive Time and Distance

Early estimates suggested that iron NPs can remain reactive in groundwater systems for in the order of 4-8 weeks and can flow with the groundwater for > 20 m (Zhang 2003). However, more recent work by Lowry and his colleagues indicated that iron NPs could remain active for longer periods, in the order of 6 months (Liu & Lowry 2006, Phenrat *et al.* 2009a). Largely due to the inability of monitoring technology to adequately track the

injected particles, field evidence reporting distance travelled by particles is relatively poorly represented within literature studies. Although iron NPs may not achieve widespread distribution in the subsurface due to agglomeration prior to complete dispersion within the soil or groundwater matrix, limiting the radius of influence, few literature studies are prepared to speculate on distances travelled. Even with surface modifications that increase mobility and decrease the zeta potential, Saleh *et al.* (2008) speculates that iron NPs are not predicted to travel much farther than 100 m from an injection location and much shorter distances when site conditions limit mobility.

While the detection of injected nZVI for example in slurry is acknowledged to be an expensive and problematic issue current research and pragmatism are bearing some useful results. One vendor has resorted to selling their own "nZVI Tester"[6]. Recently de Boer *et al.* (2009) reported column experiments in which they observed a 2 m radius of symmetrical injection of iron NPs. They also observed a delayed breakthrough of iron NPs compared with a conservative tracer. A surfactant was added by the iron NPs producer to prevent sedimentation of the suspended iron NPs.

Henn and Waddill (2006) report that *"Some of the particles flow with the groundwater and remain in suspension for various amounts of time, whereas others are filtered out and bind to soil particles, providing an in situ treatment zone that could hold back emanating plumes".*

4.3.4 Iron NPs and Biota

The influence of iron NPs on soil microorganisms, and *vice versa*, is much less well understood, as well summarised by Wiesner *et al.* (2006): "*Redox reactions are often mediated by microorganisms, either directly through enzymatic activity or indirectly through the production of biogenic oxidants (e.g., reactive oxygen species (ROS) produced by lignocellulolytic fungi) or reductants (e.g., surface-associated Fe(II), a common abiotic reductant in natural systems that can be produced by iron-reducing bacteria). Whether nanomaterials could be transformed to an appreciable extent by such abiotic redox processes in the environment is unknown and would likely depend on the thermodynamic feasibility and kinetic facility of the electron transfer".*

The consequence of such interactions could be to affect the efficiency of the iron NP treatment but also to hinder the effectiveness of some natural processes. For example "*Macé et al. (2006) noted minor but inconclusive changes to the microbial community due to the addition of nanoparticles. These changes could affect parallel bioremediation"* (Karn *et al.* 2009). Another contributory parameter of influence on the toxicology is clearly the dose quantity. Barnes *et al*. (2010) report cytotoxicity of 100 mg/L nZVI to bacterial cells in microcosm experiments using river water. However the relevance of this finding is questionable in the context of realistically occurring concentrations since the UK drinking water standard for iron is some 500 times lower at 200 µg/L.

Nevertheless, field evidence is tending to show an overall synergistic effect between injected nZVI and the microbial consortia responsible for anaerobic biodegradation. When injecting nZVI to treat chlorinated solvents in groundwater, we often see both the abiotic reduction of target compounds and then see the biological anaerobic signature (D.W. Elliott 2010). Studies in the literature by Kirschling *et al.* (2010) and Comba *et al.* (2011)

[6] http://www.nanoiron.cz/en/nzvi-tester

both indicate that microbial processes related to dehalogenation of solvents can continue and even be enhanced in the presence of iron NPs.

4.3.5 Colloids

Depending on the composition of groundwater and the hydrologic conditions, certain nano-scale colloids have the ability to travel unexpectedly large distances in the environment (Kersting *et al.* 1999; Novikov *et al.* 2006; Vilks *et al.* 1997). Naturally occurring nano-scale iron oxide particles with metals (such as copper) bound to their surface have been found many kilometres downstream from mining sites, indicating the ability of these colloidal nanoparticles to move and transport sorbed contaminants (Hochella *et al.* 2005). Iron nanomaterials may bind with and carry copper, which has a toxicity threshold for algae, flowering plants, fungi, and phytoplankton that is surpassed only by mercury and sometimes silver (Sposito 1989). Formed, stable nanoclusters in groundwater that are likely to be highly mobile, carrying with them surface-sorbed contaminants are discussed for their secondary contaminant transport risks in Section 4.5.5. These natural particles can carry materials between redox zones and facilitate or inhibit contaminant transport (Waite *et al.* 1999).

In addition to self-agglomeration, nanoparticles could associate with suspended solids or sediment, where they could bioaccumulate and enter the food chain or drinking water sources. These fate processes depend on both the characteristics of the particle and the characteristics of the environmental system (Boxall *et al.* 2007).

Karn *et al.* (2009) summarises: *"Although aggregated and/or absorbed nanoparticles are usually less mobile, they still have the potential to be taken up by filter feeders and other sediment-dwelling organisms. The U.S. EPA has raised the possibility of biomagnification of nanoparticles; however, no data currently exist proving or disproving this hypothesis (Biswas and Wu 2005; U.S. EPA 2007). To be able to quantify the stability of nanoparticles in the environment, the stability of their suspensions and their tendency to aggregate and interact with other particles must first be determined (Mackay et al. 2006)".*

Colloids have also been implicated in the transfer of radionuclides (McCarthy and Zachara 1989; Hoffman 2002). Nevertheless there are difficulties in studying fine particles as illustrated by Kung (2000) who found both that colloids were unstable during storage and could be introduced during storage, filtration and dilution processes. Kung recommended that analysis of colloid size and composition should be carried out soon after sample collection. Indeed, Karn *et al.* (2009), states that the fundamental agglomeration and transport properties of nanoparticles have not yet been extensively studied.

4.4 Toxicity of Iron NPs

This section of the report looks into the sometimes conflicting scientific literature regarding toxicological and ecotoxicological effects of iron NPs, which is reviewed in the context of the toxicity of the contaminants iron NPs is deployed to remediate. While the absence of evidence is not evidence of absence, a reluctance to adopt a 'lines of evidence' approach can result in an overly cautious stance.

Iron is an essential element for growth in nearly all species as well as being an essential nutrient whose deficiency can result in abnormally low red blood cell counts and associated symptoms. Keane (2009) reminds us that naturally occurring NPs containing iron are ubiquitous. Iron can nevertheless be toxic in excess, Valko *et al.* (2005). Zero-valent iron (ZVI) exhibits different properties and behaviour to naturally occurring iron

forms (Fe^{2+} and Fe^{3+}) and whilst used in PRBs for groundwater remediation, it is these properties which, in combination with the nano scale, are key to its hazard potential.

4.4.1 Uncertainty Background

The toxicity of nano-scale iron to human beings and other organisms, its modes of uptake and its metabolism are poorly understood. The uncertainty of the dose-response relationship between human health and iron NPs has been acknowledged (IAHS 2002) and no subsequent evidence has suggested that anything other than a precautionary approach to any studies would be sensible. However, the toxicology of conventional ZVI already used in remediation also appears to be poorly understood (Keane 2009).

Watlington (2005) surmised that concerns regarding the toxicity of the technology have been mild, stating confidence in safety is largely due to the fact that *"iron oxides formed during remediation are already present in the ground as rust, coupled with the fact that iron NPs do not exhibit radically new properties"*. However this study was published when no studies reporting the safety and toxicity of iron NPs or bimetallic particles had yet been published. Boxall *et al.* (2007) summarises with a similar albeit more cautionary line, acknowledging the environmental and human health risks are probably low "*our knowledge of the potential impacts of engineered nanoparticles in the environment on human health is still limited"* and stating the need for targeted research on exposure levels.

Concerns regarding the toxicity of iron NPs could be broadly split into those relating to the particles nano-scale size and those relating to the toxicological effect of the actual iron. With respect to human health, studies have shown effects but not necessarily adverse effects as a result of the size rather than composition or enhanced chemical reactivity of nano particles. Although their document does not consider iron NPs *per se*, Renn and Rocco (2006) provided a good overview of the specific issues, concluding that: *"Several studies have shown that: (i) due to the high surface-area-to-volume ratio and higher reactivity of nanostructures, large doses can cause cells and organs to demonstrate a toxic response (in particular inflammation) even when the material itself is non-toxic; (ii) some nanosized particles are able to penetrate the liver and other organs and to pass along nerve axons into the brain; (iii) nanomaterials may combine with iron or other metals, thereby increasing the level of toxicity and presenting unknown risks; (iv) engineered nanomaterials raise particular concerns because of the unknown characteristics of their new properties and their potential use in concentrated amounts; and (v) some nanomaterials may have similar characteristics to known high-risk materials at the microscale"*. Crucial to these toxicological issues is the point at which the iron NPs core becomes covered by a thin film of iron oxides, transforming the particle to a so-called passive state.

4.4.2 Passivation of Iron Nanoparticles

In terms of evaluating toxicity of iron NPs, there is a clear distinction in terms of particle behaviour and crucially, toxicology, from the point when an unreacted iron NP becomes passivated. Passivation may occur through the reaction of iron with contaminants, groundwater constituents such as nitrate and dissolved organic matter, the subsurface matrix and the agglomeration of iron NPs. Sorption and agglomeration processes may be partly reversible.

Reacted or passivated iron NPs appear to be relatively benign to bacteria - principally based on tests using *Escherichia coli* (Auffan *et al.* 2008, Li *et al.* 2010, Phenrat *et al.* 2009a).

Keane (2009) acknowledges that iron oxides (a likely passivated form of partially reacted iron NPs) can accumulate to a level that cause adverse effects to bacteria, mammalian nerve cells, fish and viruses, despite being an essential nutrient. It should also be remembered that iron NPs in the groundwater environment exhibits a core-shell structure in which the outer "shell" is comprised of iron oxyhydroxides or carbonates, the specific composition of which is a function of solution geochemistry while the interior "core" is largely zero-valent iron. Over time, the shell tends to expand while the core shrinks but as Lui & Lowry (2006) found, core reactivity can remain for a period of several months or longer. It is suggested that agglomerated and/or absorbed iron NPs (although less mobile) still have the potential to be taken up by filter feeders and other sediment dwelling organisms. Karn *et al.* (2009) concludes that research is yet to substantiate the stability of iron NPs, their tendency to agglomerate and interaction with other particles which will better conclude how much potential risk this suggested exposure linkage would provide.

4.4.3 Literature Evidence

Weisner *et al.* (2006) report the potential for negative health effects from exposure and uptake of nanoparticles into mammalian cells. However they also concede that studies are *in vitro* responses and are at significantly higher exposures than expected from probable environmentally relevant concentrations.

Iron NPs have been found to be toxic to bacterial cells *in vitro* (Auffan *et al.* 2006, Li *et al.* 2010). This toxicity exceeds conventional iron *in vitro* toxicity (Lee et al, 2008). A number of laboratory based studies have indicated that at higher than prevalent background concentrations iron NPs may be toxic to particular soil and groundwater organisms (Barnes *et al.* 2010), however it is also clear that aquifer microbial processes related to dehalogenation of solvents can continue and even be enhanced in the presence iron NPs (Comba *et al.* 2011). Kirschling *et al.* (2010) found that in microcosms on aquifer material, nZVI addition had no deleterious effect on total bacterial abundance. Barnes *et al.* (2010) based on microcosm studies of river water microbial community in the presence of iron NPs found that addition of iron NPs did not influence bacterial community structure, although they did find short term perturbations.

Keenan *et al.* (2010) found limited oxidative stress and cell damage induced by iron NPs, from laboratory tests using human bronchial epithelial cells.

Sayed El-Temsah *et al.* (2010) used seed germination to test the bioavailable iron NPs toxicity in aqueous solution and in two different soil types. Although inhibitory effects of the nZVI were observed at higher concentrations, the study concluded that iron NPs at low concentrations can be used "without detrimental effects on plants and thus be suitable for combined remediation where plants are involved".

In vitro tests have identified that iron NPs 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 (Blaise *et al.* 2008, Brunner *et al.* 2006, Eun and Myung 2007, Keenan *et al.* 2009). The significance of this from the point of view of understanding toxicity from the environmental applications of iron NPs is unclear. For example, dose-response relationships may be uncertain (Limbach *et al.* 2007), and Auffan *et al.* (2009) found that chemically stable metallic NPs have no significant cellular toxicity. Phenrat *et al.* (2009a) found that partial or complete oxidation of iron NPs reduced their toxicity to mammalian cell lines. Furthermore, iron NP cellular toxicity is not reported for some *in vitro* studies (Hildebrand *et al.* 2010). Iron oxide NPs also have *in vivo* medical applications and food sector applications (Lewinski *et al.* 2008, Chaudry and Castle 2011), although, again, there are some uncertainties about their use in these applications.

Other workers have also commented on the paucity of our evidence base while at the same time reporting cellular level adverse effects: "*In some cases, Fe oxide nanoparticles (a potential end product from redox reactions of iron NPs) can be internalized by cells and cause cell death. Low solubility of Fe oxide nanoparticles enables them to persist in biological systems and could potentially induce long-term effects involving mutagenic influence on organisms"* (Auffan *et al.* 2006). However, there are limited data on the interactions of Fe oxide nanoparticles with cells and the effect that coatings can have on cell adhesion, internalization, and interaction.

4.4.4 Impact from Other Nanoparticle Constituents

Wiesner *et al.* (2006) consider the issue of surface coatings of nanoparticles, stating that to effectively deliver iron NPs for *in situ* groundwater remediation, *"unique surface coatings will be required to make the particles mobile in the subsurface; these modifications may in turn increase their potential for unwanted exposure to humans and other organisms"*.

While this review only considers nZVI, it should be pointed out that nZVI can be coated with other potentially more toxic substances for the purposes of enhancing reactivity or improving stability (i.e. lessening the extent of agglomeration). *"Typically, a noble metal (e.g., palladium, silver, copper) can be added as a catalyst. The second metal creates a catalytic synergy between itself and Fe and also aids in the nanoparticles' distribution and mobility once injected into the ground (Saleh et al. 2007; Tratnyek and Johnson 2006; U.S. EPA 2008b)"* quoted by Karn *et al.* (2009).

Accordingly, toxicity from the iron NP preparations could also include the toxicity of any non-iron trace metal catalysts used in some types of nanoparticle, such as palladium. Although the percentage of palladium in the injected iron NP mass is extremely low, typically around 0.1% (1,000 ppm), this consideration should also be taken into account if iron NPs are employed with catalysts. Few toxicological studies have been carried out, but Hildebrand *et al.* (2010) found a limited toxicological effect of palladium doped nano-scale iron oxides on cell lines of human skin, the human colon, and trout gills.

In general generic risk based thresholds for the precious metals typically used for doping iron NPs in bimetallic nanoparticles (BNPs) do not exist. However, for the elements used in nano-iron Dutch "intervention" values range between 10 to 100 ppm (Dutch Soil Remediation Circular, 2009), i.e. a level above which remediation of a site would have to be considered. Assuming transport of BNPs laterally and downwards 1 m from an injection point and a bulk density of soil of 1.7 tonnes per m^3 (dry weight). This means that an accumulation of BNPs in soil at 1-10% (17 – 170 kg) the intervention levels would be exceeded. With BNP concentrations used for injection of several grams/L (kg/m^3) exceedance is unlikely to occur.

Materials may also be added to iron NPs to improve their stability or other functions, as described in Section 2. These are generally non-toxic materials, such as biodegradable polymers. However, some amendments, such as particular surfactants, may be toxic in the environment. The practical significance of this is uncertain, for example, such as the type of surfactant and the amount typically employed. Moore (2006) speculates on the potential ecotoxicity of nanomaterials and recommends *"individual evaluation of new nanomaterials for risk to the health of the environment"*.

Surface-modified nanoparticles have been developed in the U.S. with various polymeric and surfactant architectures to lessen agglomeration and enhance stability. Such

coatings are much rarer in the environment and probably merit more of the concerns raised above with respect to nZVI.

4.4.5 Secondary Risks

Renn and Rocco (2006) point out another potential risk linkage, not from the toxicology or accumulation of iron NPs, but with them creating a vehicle for other potential secondary contaminant accumulation. Iron NP absorption of contaminants (e.g. pesticides or cadmium), is cited as a mechanism by which non-biodegradable contaminants could bioaccumulate and conceivably be transferred on into the food chain. Stable nanoclusters can carry materials between redox zones and facilitate or inhibit contaminant transport (Waite *et al.* 1999).

It is known that, stable nano-scale colloids, depending on the composition of groundwater and the hydrologic conditions, have the ability to travel unexpectedly large distances in the environment (Kersting *et al.* 1999; Novikov *et al.* 2006; Vilks *et al.* 1997). Naturally occurring nano-scale Fe oxide particles with metals (such as copper) bound to their surface have been found many kilometres downstream from mining sites, indicating the ability of these colloidal nanoparticles to move and transport sorbed contaminants (Hochella *et al.* 2005). The significance of this process for iron NP use in practical remediation appears to be unknown.

Undoubtedly exposure and uptake of some forms of nanoparticle do occur, however the severity and undesirability of the consequences of such uptake are poorly understood as described by Moore (2006): *"Inorganic [ceramic] nanoparticles have been identified in human liver and kidney tissues (Gatti and Rivasi 2002). These authors coined the term "nanopathology" and believe that these particles, which are of exogenous (ceramic?) origin, could have a causal link with cryptogenic granulomas in the tissues examined. In aquatic and terrestrial invertebrates, metalliferous nano and microscale granules are frequently found in cells of digestive and excretory tissues (Viarengo and Nott, 1993). Nott and Nicolaidou (1990) have developed models for the formation of these granules, some of which are related to the lysosomal system, and their role in the sequestration, detoxication and biomineralisation of toxic metals such as iron, copper, mercury, lead, silver, chromium and nickel (Nott and Nicolaidou, 1990; Viarengo and Nott, 1993)"*.

It is important to note that Gatti and Rivasi's findings concerned the presence in the kidney (<6 µm) and liver (<20 µm) of *"a silicate of aluminium, magnesium, sodium, potassium, i.e. a ceramic material whose origin could not be but exogenous"*. Further investigations also identified porcelain and metallic dental origins, barium meal detritus, gold therapy and bioptic sampling artefacts but not from orthopaedic prosthetics.

In reviewing the origins of nanopathology, Moore (2006) grouped iron with other widely recognised contaminants: *"toxic metals such as iron, copper, mercury, lead, silver, chromium and nickel"* without obviously recognising that iron is an essential component of red blood cells and that it is inherently much less hazardous than the other substances listed[7]. Interestingly Gatti and Rivasi coin the term nanopathology to refer to *"non-degradable micro and nanoparticles"* and mention a 20 µm threshold below which an ingested particle *"can pass through the intestinal barrier and is likely to end up in the bloodstream"*.

[7] Example Material Safety Data Sheets for Iron NPs:
http://www.nanoamor.com/i/u/300402/h/MSDS/MSDS_Fe_8001NJ.pdf;
http://www.hepure.com/msds/msds-hc15.pdf

Gatti and Rivasi (2002) conclude that the likelihood of a nanoparticle pathology's origin may depend upon the presence of inorganic particles that cannot be metabolised or disposed of. However, once particulate iron is ingested and migrates to the low pH stomach environment, it will end up in an ionic form. Therefore as an essential nutrient particulate iron can be metabolised.

Wiesner *et al.* (2006) report that *"metal and metal-oxide nanoparticles (e.g., nanoiron, magnetite, TiO_2) have been proposed for groundwater remediation, water treatment, and removal of toxic contaminants from air streams"*. Whilst they do not list any iron containing substances among the studied cytotoxic nanomaterials, they do present a transmission electron micrograph of a microglia cell in which black areas are interpreted as assimilated iron NPs. *"Preliminary investigations of the in vitro response of central nervous system (CNS) microglia to low concentrations of nanoiron (2–30 ppm) and nanomagnetite (2–30 ppm) indicate that these nanoparticles produce an oxidative stress response and are taken up into cells. Noncytotoxic doses of Degussa P25 nano-TiO_2 caused rapid and sustained release of ROS by CNS microglia, indicating the potential for neurotoxicity. Exposure to these nanoparticles also affected ATP levels, caused mitochondrial depolarization, and stimulated an oxidative burst in the microglia and neurons. These results suggest the potential for negative health effects from exposure and uptake of nanoparticles into mammalian cells. However, it is important to note that these are in vitro responses and represent significantly higher exposures than expected. Toxicity data and the potential exposure levels must be considered simultaneously to determine the risks"*. (Wiesner *et al.* 2006)

4.5 Ecotoxicity

4.5.1 Accumulation

The ecotoxic effects of nanoparticles will depend on the composition of the particles, including any coatings, the particle size and the target organism. Keane (2009) reviews iron NPs toxicity to bacteria, mammals (mammalian nerve cells), fish and viruses. She recognises iron is an essential nutrient but goes on to point out that iron *"can accumulate to a level that causes DNA damage, oxidative stress, lipid peroxidation, and severe diseases such as hemochromatosis and carcinogenesis"*. However she admits that most studies have considered Fe^{2+} and its oxides rather than elemental iron and little is known about the toxicity of nano or macro ZVI.

4.5.2 Properties from Synthesis

Some authors have speculated that the genesis of nano particles may bequeath them different toxic potential. *"Handy et al. (2008) suggested that despite the environment containing many natural particles at the nano-scale, manufactured nanoparticles may act differently. These materials are designed to have specific surface properties and chemistries that are not likely to be found in natural particles. The properties of manufactured nanoparticles enhance novel physicochemical and possibly toxicologic properties compared with natural particles"* (Karn *et al.* 2009). Oberdorster *et al.* (2006) reported that *"the testing of the Reactive [sic] Nano-Iron Particles revealed no significant toxicity issues for the material, though the tests are not all-inclusive since only two species were studied, and only 2000 genes are printed on the DNA array. However, data of this type can serve to quickly highlight toxic materials and can serve as a basis for more detailed mechanistic studies".* Golder Associates (2009) interpreted these findings as suggesting that iron NPs had the same ecotoxicity (48 hour LC50) as bulk macro ZVI used in PRBs and would classify iron NPs as 'slightly toxic'. They also refer to the then

imminent Auffan et al. (2009) paper, now published in *Nature Nanotechnology,* discussed directly below.

4.5.3 Size Dependence

Auffan *et al.* (2009) proposed a sub division of nano particles into those smaller and larger than 30 nm. They found that the larger nano particles essentially behaved and should be regulated as their bulk counterparts. However those nano particles smaller than 30 nm *"have a size-dependent crystallinity that gives them properties drastically different from the bulk material"*. This is not a problem in reality as most iron NPs applications are in the 60-100 nm size range. Lee *et al.* (2007) also studied small nanoparticles (<46 µm) but of silver and found they penetrated, via passive diffusion, zebrafish embryos and caused harm up to death with increasing dose. They reported a critical concentration of 0.19 nM silver and also proposed the use of zebrafish embryos as a bioassay for biocompatibility and toxicity studies of nanoparticles. Lee *et al.* (2007) also speculate that *"the release of large amounts of Ag nanoparticles into aquatic ecosystems (e.g., rivers) may have drastic environmental consequences, should the sizes of nanomaterials remain unchanged during environmental transport"*.

Iron NPs have been found to have bactericidal effects against *Escherichia coli* (Lee *et al.* 2008). However, Li *et al.* (2010) found that iron NP bactericidal properties against *E. coli* were mitigated if the iron NPs were oxidised or were sorbed to polymers or natural organic matter. Auffan *et al.* (2008) found that oxidised iron NPs were not toxic to *E.* coli. Dissolved oxygen very rapidly oxidises iron NPs to various iron oxides (Reinsch *et al.* 2010). Kirschling *et al.* (2010) found in microcosm trials that iron NPs had no deleterious effects on bacterial reduction of trichloroethene (TCE) but did change the composition of the bacterial community. Furthermore, adding iron NPs with a biodegradable polyaspartate coating (See Section 2.2) increased bacterial populations by an order of magnitude relative to controls.

4.6 Human Exposure to Iron NPs

Exposure to iron NPs may take place through dermal contact, ingestion or inhalation. In a remediation context, dermal contact is unlikely due to the almost ubiquitous use of PPE. Accidental contact could result in iron NPs passing into and harming cells.

Ingestion is possible if normal hygiene precautions are ignored or if iron NPs injection contaminates groundwater wells. However the high toxicity of the halogenated contaminants being also remediated make this exposure route highly unlikely: wells are not going to be producing water for consumption in an aquifer known to be polluted with chlorinated solvents.

Inhalation is a potentially more significant exposure route for nano rather than larger sized particles. Karn *et al.* (2009) report that *"Research on ultrafine particulates (< 100 nm in one dimension) has shown that as particle size decreases, potential for pulmonary toxicity tends to increase even if the material's larger form is inert. Iron NPs are typically between tens and hundreds of nanometers in size at the time of production. Under laboratory conditions, these particles tend to aggregate and produce clusters that can build up to the micrometer size. If this occurs, they will not take on the properties that apply to actual nanosized particles and will behave similarly to larger environmental colloids (Tratnyek and Johnson, 2006)"*. Karn and her co authors go on to explore the evidence of effects caused by inhalation: "*Inhalation exposure to* $Fe^0(s)$ *nanoparticles could result in the release of Fe(III), followed by oxidative damage due to generation of Fe(IV) (Keenan and Sedlak 2008). In vitro [sic] studies examining the response of the central nervous system*

to low concentrations of nano-Fe and nanomagnetite showed that these nanoparticles are taken up into cells and produce an oxidative stress response (Wiesner et al. 2006). These studies indicate a potential for adverse health effects from exposure and uptake of Fe oxide nanoparticles into mammalian cells. The authors caution, however, that these tests were conducted at much higher dosages than would be encountered normally (Wiesner et al. 2006)". This observation suggests the need for good, robust, above ground handling techniques.

Inhalation is not a relevant exposure route for iron NPs delivered to site in the form of a slurry. It is more relevant when iron NPs are delivered as a dry powder and would be mitigated by handling precautions that are routine for other chemicals such as those used for *in situ* chemical oxidation.

Overall there has been little research into the toxicity of nZVI but rather more on other nanoparticles. What research has been reviewed suggests that iron NPs are one of the more benign nanoparticles. However the toxicity of coated iron NPs is substantially and significantly different and probably greater than that of uncoated iron NPs. In comparison with the toxicity of the contaminants iron NPs are deployed to remediate, uncoated iron NPs are highly unlikely to be as toxic and even coated iron NPs do not seem likely to be of similar toxicity.

Given the uncertainty of the dose-response relationship between human health and iron NPs, a precautionary approach to any studies would be sensible. The potential for exposure at the various stages of using iron NPs for remediation is significant in the absence of suitable protection measures (Table 6). No evidence on the anticipated exposure levels has been found in the literature.

Table 6: Potential for Human Exposure to NPs (Assuming no personal protection measures)

Activity	Ingestion	Inhalation	Dermal
Manufacture	Low	High	Moderate
Transport	Low	Low	Moderate
Storage	Low	Low	Low
Deployment	Low	High	High
Operation	Low	Low	Low
Spill	Low	Low (with PPE)	High
Decommissioning	Low	Low	Low

Nevertheless the overall benefits of using iron NPs do seem to suggest that the effort in deepening our understanding, and mitigating the adverse effects of such exposure is worth expending: *"The average pump-and-treat system operates for about 18 years (U.S. EPA 2001). In a study using nZVI, Zhang (2003) observed a 99% reduction in TCE levels within days of injection. This shortened time interval not only reduces operating costs but also reduces the time that workers are exposed to a contaminated site during cleanup".* (Karn *et al.* 2009).

"Currently, there are no specific exposure limits for airborne exposures to engineered nanoparticles although occupational exposure limits exist for larger particles of similar chemical composition." (QuantumSphere, Inc. 2007).

At the very least a basic dose-response relationship for nZVI or an occupational exposure level is required.

4.7 Perceived Risks of Releasing Iron NP into the Surface and Subsurface Environment

The considerable public wariness with new technologies coupled with acknowledged gaps in our present understanding of nanomaterials has resulted in many reports of perceived risks (Nowack 2008). These need to be acknowledged and addressed if the benefits are to be fully realised. The perceived risks from iron NPs of many academic commentators and NGOs revolve around a lack of research (e.g. Boxall *et al.* 2007, Nowack and Bucheli 2007, Wiesner *et al.* 2006). Scientific concerns have been voiced about the differences between micro- and nano- particles and the easier penetration by nanoparticles into human tissue (International Risk Governance Council 2006). However what commentary there is suggests that the perceived risks are likely to be much higher than the real risks. There are several recommendations for additional research to confirm the suspected low toxicity of iron NPs to humans. Some, such as the Royal Society, can take a hard precautionary approach. Others may delay adopting iron NPs due to potential reputational risks. Perceptions are therefore an important hurdle for users of environmental nanotechnology, and will need to be addressed with a sound evidence base, and a cautious approach to their adoption.

Karn *et al.*(2009) supports this view stating *"The consensus is caution, not precaution, and, in the absence of definitive risk data, the technology is generally viewed as more beneficial than harmful".*

Major corporations are adopting a cautious approach, perhaps reflecting a desire to avoid any adverse reputational impact for example the position of the Du Pont corporation previously mentioned, where they decided Du Pont "*would not consider using this [iron NP] technology at a Du Pont site until the end products of the reactions following injection, or following a spill, are determined and adequately assessed".* This remains their position (D.W. Ellis 2011 pers. comm).

The Royal Commission on Environmental Pollution (2008) cited in Karn *et al.* (2009) stated that the risks to nZVI will be considered in the context of previous attempts at introducing new technologies in to the environment: *"While there have been no significant events that would lead us to suppose that the contemporary introduction of novel materials is a source of environmental hazard, we are acutely aware of past instances where new chemicals and products, originally thought to be entirely benign, turned out to have very high environmental and public health costs".* (RCEP 2008, cited by Karn et al. 2009).

4.8 Risk Appraisal

Keane (2009) concludes "*Responsible use of iron NPs in environmental applications and careful management of the associated risks requires a fundamental understanding of their mobility, potential bioavailability/bioaccumulation, and impacts on a wide variety of organisms. Currently this fundamental understanding of the environmental fate of iron NPs and their oxidation products is not well understood for the variety of environmental conditions that may occur*."

Iron NPs can pose health and safety risks if improperly handled. There is evidence that they can be hazardous to human health and other organisms. The exact scale of direct

and secondary risks is as yet not established. However, the implication is that unreacted iron NPs are so distance constrained from the point of deployment that suitable site selection for pilot trialling/treatment could easily overcome the threat of reaching certain receptors. Furthermore, reacted iron NPs appear relatively harmless in the environment. Whilst this view appears prevalent with those demonstrating the application of iron NPs, it is not yet categorically substantiated in the field (D.W. Elliott 2010 pers. comm.). What is more clear is the lessened potency of reacted, or passivated, iron NPs which become larger by virtue of agglomeration and interaction/removal by the aquifer media, and its outer exposed portion becomes a complex mixture of iron oxyhydroxides whose precise composition will vary depending upon the local lithology and geochemical conditions in the groundwater. These larger particles are subject to more rapid stabilisation by the aquifer matrix.

Any impact on aquifer microbiology would likely be both in the treatment zone and in a halo surrounding it, related to the ability of iron NPs to migrate further. This “halo” may be relatively slight given the penetration of iron NPs in aquifer materials, unless for example, the iron nanoparticles were sufficiently well coated and suspended within emulsified liquid denser than groundwater.

5 RISK BENEFIT

5.1 Risk-Benefit Appraisal

The UK Nanotechnologies Strategy (HM Government 2010) recognises the role of government in encouraging a 'cohesive and flourishing industry' while "also acknowledging and addressing the implications for health, safety and the environment". The need for public confidence in nanotechnology was highlighted and active engagement with the public was seen as essential in developing such confidence. This is particularly important for technologies involving the release of nanomaterials into the environment (RCEP 2008), as would be required for *in situ* remediation purposes. Section 4.3 underlines how risk perception as well as the "reality" of risks affects the adoption of nanotechnologies. This needs to be acknowledged and addressed if the benefits Government foresees from nanotechnology are to be realised.

Section 4.3 concludes that perceived risks are likely to be much higher than the real risks, although attitudes vary. Perception also has a corporate impact. Annex 1 describes the position of many UK practitioners in their likely adoption of iron NP based remediation. Section 4.7 describes the view of Du Pont (a major contaminated site management and technology business) who have not adopted iron NP remediation owing primarily to a present absence of toxicological health evidence.

In practice the use of iron NPs has not yet delivered the step change in remediation performance perhaps envisaged by some of its proponents. However, where adopted, it has become an important niche technology for *in situ* chlorinated solvent treatment that is compatible with, and indeed may enhance, anaerobic biological processes of dechlorination. The prevalence of chlorinated solvent problems and their intractability is a significant market opportunity, which appears to be the driver for this focus in the use of iron NPs.

The observation that practical use of iron NPs has largely been for chlorinated solvent remediation does not invalidate the proposition that iron NPs may facilitate important improvements in remediation capability. Laboratory-scale findings indicate opportunities for treating biologically recalcitrant contaminants (such a chlorinated aromatics); and *in situ* stabilisation of some important inorganic contaminants, particularly those existing in oxidised anionic forms. However, by and large, these have yet to evolve into widely used practical remediation techniques.

Iron NPs are known to be hazardous to prokaryotic and eukaryotic cells, although this hazard appears to be substantially reduced for reacted or passivated forms of the iron NPs. However, compared with environmental contaminants such as trace elements, little information is available about their toxicology, mode of action, exposure pathways of iron NPs (or their products) for human health or environmental receptors.

This lack of knowledge needs to be addressed through research (Table 9 summarises suggested research needs), but does not militate against permitting the use of iron NPs in the UK. Use in the field in other countries indicates that risks from iron NPs, including many modified forms, are manageable, since their persistence in the environment appears to be relatively short (< 1 year), and their ability to travel from injection points is limited (1 to 100 m for some modified types).

What should not be overlooked is that other remediation techniques carry risks. The simplest remediation technique is excavation and removal, and this carries risks from

operating plant and machinery as well as road traffic, which have been successfully used to argue against extensive "dig and dump" remediation proposals (Wallace in NICOLE, 2009). Operator health and safety has been raised as a concern for iron NP use. However, these can be addressed by conventional good practice, and more hazardous redox agents are used in the subsurface, in particular Fenton's Reagent based on hydrogen peroxide. *In situ* chemical oxidation using a Fenton's reagent approach was responsible for the only known fatalities from an *in situ* remediation operation (ITRC, 2001). Other *in situ* redox reagents that are used (Nathanail *et al.* 2007, US EPA 2006) include permanganate and persulphate. These alternatives are potentially harmful for the biological functioning of soil, but are conceivably available for use in the UK. It should also be borne in mind that these are oxidation agents, whereas iron NPs are reducing agents, hence their functionality in remediation is different, although they may be applied to similar problems such as NAPLs and more specifically, halogenated volatiles, semi-volatiles, PCBs and non-volatile metals.

The other major competing degradation based technology to iron NPs for chlorinated solvents is *in situ* bioremediation which depends on the injection of an organic substrate into the subsurface. Both *in situ* bioremediation and *in situ* use of iron NPs cause perturbations in the subsurface environment to mediate their remediation effect, for example altering oxidation potential and pH. Additionally, *in situ* bioremediation introduces organic substrates into aquifers, which in some cases such as vegetable oils, may be quite long lived.

Extractive technologies are also applied for NAPL treatment *in situ* in the UK, for example flushing with surfactants and heating. Surfactants can damage soil structure (Nathanail *et al.* 2002). Damage by heat may have widespread impacts on soil functionality.

Hence, a potential asset for iron NP use may be a lowered impact on soil functionality compared with many competing technologies. However, the importance of soil functionality will of course depend on the end use for which a site is destined.

Friends of the Earth (2010) have raised questions about the sustainability of nano-material production and use in general, in particular its energy intensity and use of resources. These are potentially valid concerns for the use of iron NPs *in situ*. Within the UK this question can be addressed within a wider concept of sustainable remediation using the SuRF-UK *Framework for Assessing the Sustainability of Soil and Groundwater Remediation* (CL:AIRE 2010) which is also described in Section 3.9.

Overall iron NPs offer an effective remediation technique for chlorinated solvent problems, with the potential for a wider range of remediation effectiveness. While there are some significant technical uncertainties about its behaviour in the environment and its impacts on organisms; practical indications are that risks are limited and manageable. Furthermore, the risks posed by iron NPs, while different, do not necessarily lead to a view that it is inherently "more risky" than existing remediation technologies. Indeed, soil and water impacts may be more benign compared with some remediation techniques already in use.

Sections 5.3, 5.4 and 5.5 discuss the site and project-specific key parameters that can, to some extent, be controlled through parameter selection and thereby dictate case-specific risks. Many of these parameters, which are split into 'source', 'pathway' and 'receptor' categories, are controlled through suitable site selection.

5.2 Source

5.2.1 Type of Deployment / Application

In the first instance the mode of deployment will determine the iron NP source term. At one extreme the iron NPs may be applied within a partially contained permeable reactive barrier, and at the other injected directly into the aquifer matrix. There will be gradations between these such as materials injected into a specific formation such as by hydrofracture. Section 2.3 discusses the various types of iron NP deployment. Injection methods range from the relatively passive, such as gravity injection, to aggressive invasive such as pneumatic fracturing followed by pneumatic injection. The degree of particle containment within each application type will determine the extent to which iron NPs might be liberated into the wider environment, and should therefore be a factor in risk assessment considerations.

Specific and unique site conditions are likely to determine the usefulness and influence the fate and transport of iron NPs during remediation efforts. The key will be a sound understanding of the fate and transport of iron NPs at each site to ensure remediation objectives are achieved while negative impacts are avoided. Poor understanding has the potential to undermine both. Factors to consider prior to application include: effects of geochemistry on the mobility of iron NPs, use of metal catalysts and coatings on the movement of iron NPs and other variables affecting the fate and transport of iron NPs in the environment (U.S. EPA 2009). Furthermore the way the iron NPs are injected into the ground (the administration method) will influence the extent to which above ground release and therefore worker and bystander exposure is possible.

5.2.2 Deployed Mass of Iron NPs

The mass of material deployed will be based on some form of calculation relating to the contamination that has to be treated. The mass deployed is likely to be well in excess of that stoichiometrically required to achieve treatment to compensate for interactions between the iron NPs and the subsurface environment, particularly as water is a reductate for iron NPs. The scale of this excess in comparison to the capacity of the subsurface environment to degrade this excess iron NPs input will be another important risk assessment consideration.

5.2.3 Type of Iron NP

Potential reactivities are different for each type of iron NP and also dependent on their surface modifications (Huang *et al.* 2008, Prakash *et al.*, 2005). Reactivities can be different for different manufacturing batches and particle storage can also affect particle reactivity. Realised reactivities are also a function of subsurface conditions, in particular of key water chemistry factors like solution pH, oxidation-reduction potential and the presence of other reductates or anions such as carbonate and sulphate.

As discussed in Section 3, highly reactive iron NPs tend to exhibit greater efficacy towards contaminants, especially those classes which are more recalcitrant (e.g. the chlorobenzenes). However, the same properties of high reactivity also limit the distance the particle is likely to be able to migrate in the subsurface without aggregating or reacting prior to reaching the target contaminant. Iron NPs may also be formulated with doped metals, coatings or in an emulsified form, which may alter their hazardous properties. Section 2 describes the different particle types, catalysts and coatings.

It is also important to note that there is variability among the morphology and chemical characteristics of iron NPs which will affect their fate, even if particles have the same chemical composition (Lui *et al*. 2005). Particle properties such as reactivity, mobility and shelf life can vary depending on the manufacturing process or the vendor providing the particle (Miehr 2004, US EPA 2008a).

Anecdotal evidence suggests that recently agglomerated assemblages can be broken down via vigorous mixing. However, agglomerated iron NPs stored for long periods (e.g. in the laboratory) may not be so easily broken up.

5.3 Pathway

5.3.1 Aquifer Characteristics and Groundwater Flow

Physical characteristics affecting transport include most importantly the hydraulic conductivity and hydraulic gradient that determine the quantity of water travelling through the aquifer. This strongly dictates the (non-retarding) residence time of particles being transmitted. Linked to this is the groundwater average linear velocity, which together with an aquifer's effective porosity (which describes the porosity available which is interconnected and can usefully transmit water flow) helps estimate the pathway length (NB will not be in a straight line) and also helps dictate the anticipated amount of dispersion and diffusion (i.e. the spread of the particles). The iron NP deployment itself may locally affect hydraulic conductivity and so likely migration of iron NPs to surface water receptors.

A secondary effect of the type of deployment is the possibility of change in aquifer porosity following reaction of the iron NPs and their conversion into oxides / hydroxides with build up of mineral precipitates. These precipitates derive from reactions with the local groundwater and the formation of iron corrosion products, as is also the case with conventional ZVI, (e.g. Phillips *et al.* 2003), depending on nano-iron particle concentration and the intrinsic permeability of the aquifer (lithology). In practical deployments, evidence of problems is limited (Saleh *et al*, 2007). It is more likely to be a performance problem for PRB installations in view of the likely greater iron NP mass deployed and their function in intercepting groundwater flow. Impacts from injected materials on aquifer permeability are not unique to iron NPs, and also occur with conventional ZVI and many other subsurface treatment additives (including redox reagents). Considerations for permitting should include evidence about possible aquifer permeability impacts, but in the same way as for other *in situ* remediation techniques.

5.3.2 Groundwater and Matrix Properties

The fate and transport of iron NPs within groundwater and soil is very site specific because it is highly affected by the geochemistry of a system which will in turn reflect the mineralogy and distribution of soil materials and the nature of the soil mass as well as the groundwater regime. There is much debate over whether or not iron NPs can be effectively transported by groundwater to impact an entire contamination plume, and if increasing mobility too much will add to concerns about particles moving offsite, resulting in loss of control and causing adverse impacts (U.S. EPA 2009). Geochemical characteristics in the aquifer affect the transport and fate of iron NPs along the pathway, including:

- Ionic strength which determines the potential for agglomeration (Keane 2009) and particularly Ca molar concentration, which often determine particle charge stabilisation

- Redox conditions which as well as affecting the performance of the iron NPs determine their rate of passivation
- pH
- Dissolved species (in particular nitrate and dissolved organic matter)
- The nature of the aquifer materials (i.e. the presence of surfaces that will react with / sorb iron NPs)

Iron NPs may become associated with the aquifer matrix as oxidised iron particles after reacting with contaminants. Iron NPs are applied to reductively degrade contaminants. As nano-iron generally acts as an electron donor (Fe(0) → Fe(II) or Fe(III)), it will always reduce the redox status compared to background redox conditions. If background redox conditions are anoxic (no oxygen or nitrate present) the main reaction product that can form is Fe(II) carbonates (e.g. siderite). If conditions are oxidizing along the flowpath, the original nano-ZVI or Fe(II) carbonate species are likely to oxidise as and precipitate as Fe(III) hydroxides. With subsequent lowering of redox conditions, reduction of the iron-hydroxide coating might re-expose a nano-iron surface.

5.4 Receptor

5.4.1 Distance to Receptors

Distance to the receptor clearly makes a significant difference to the likelihood of any risks being realised. By increasing the 'pathway' length, greater distance to the receptor provides the equivalent of a safety coefficient to attenuation processes such as the degree of passivation, agglomeration, filtration and sorption of the original form of iron NPs.

5.4.2 Type of Receptors and Impacts

The receptor of concern is the biology of surface water bodies which may be in continuity with and fed by the groundwater within the aquifer, groundwater source protection zones, or anywhere else understood to host aquatic life. The microbiology of groundwater could also be considered a receptor in its own right. Although this is not assumed as a default receptor for chemical or thermal treatments, in practice this would also need to be agreed up front with the regulator. Equally, plant uptake could be a possible receptor if the root zone can impinge upon the saturated zone. Potential effects on these receptors are not well understood (as discussed in Section 4).

6 KEY REQUIREMENTS NECESSARY TO EVALUATE RISKS OF USING NANOPARTICLES FOR REMEDIATION IN ORDER TO PERMIT THEIR USE

6.1 Present Regulatory Context as it Pertains to Remediation Using Nanoparticles

Under European legislation, excavated soil or abstracted groundwater is waste while unexcavated soil and *in situ* groundwater are not waste. Nevertheless, the *treatment* of contaminated soil and contaminated controlled waters, whether *in situ* or *ex situ*, may be subject to an appropriate environmental permit. Where the activity involves the injection of nanoparticles into the ground, mobile plant would be used, and the activity regulated under a Mobile Treatment Licence (MTL) in England, Northern Ireland and Wales, or by a Mobile Plant Licence (MPL) in Scotland. The provision of the MTL/MPL does not mean that the process will be suitable for meeting any remediation objectives specified under planning or other regulatory controls. The provision of the MTL/MPL controls those activities that may cause pollution or harm to human health during its operational use, and compliance monitoring will be required to ensure that pollution or harm are not caused by the remediation activity.

The Environment Agency recognises the need to exempt trials of new techniques and provides criteria for such an exemption from a MTL (Environment Agency 2010a). However there is a presumption that the trial will not cause pollution of the environment or harm. This suggests the need for extensive laboratory pilot scale studies perhaps on a site specific basis at least in the early stages of implementing iron NPs remediation coupled with ecotoxicity tests to demonstrate the benign nature of the iron NPs. Alternatively the full rigour of MTL permitting will need to be undergone even for trials.

The Environment Agency advises that only specific cases of remediation trials would meet the requirements for exclusion from the need for an Environmental Permit. Specifically excluded is the “Direct input into groundwater of the equivalent of 10 litres of any non-hazardous pollutant for the scientific purpose of groundwater testing or promoting remediation at a concentration not greater than 10 times the concentration at which it is suitable for human consumption.” (Environment Agency 2010b). It may be considered disproportionate to require an Environmental Permit for small-scale trials (such as pilot studies) or for trials of new techniques. However it is likely that both the quantity of iron NPs would exceed 10 litres and the pollutant levels in the groundwater would be more than 10 times the drinking waster standard. This of course also puts to one side the issue of whether or not iron NPs would be classed as non-hazardous. Regulatory Position Statements are used by the Environment Agency of England and Wales to preclude the need for a MTL so long as certain conditions are met, including the provision to the Environment Agency of a method statement explaining the remediation technique including full and complete details of the validation criteria; during and post treatment monitoring proposals; and supervisory arrangements that will be employed during the trial.

Also it is noted that the current REACH regulation (Registration, Evaluation, Authorisation & restriction of CHemicals) does not specifically refer to nanomaterials, but applies to substances irrespective of size or physical shape and therefore includes nanomaterials. Under REACH, manufacturers and importers have to register their substances if greater than 1 tonne per annum in volume and ensure that they do not adversely affect human health or the environment. As REACH applies to, but does not specifically give guidance on, nanomaterials, the REACH Implementation Projects on Nanomaterials (RIP-oN) were initiated to evaluate the applicability of the existing guidance and to develop advice on: substance identification (RIP-oN 1); information requirements, including testing strategies

(RIP-oN 2); and chemical safety assessments (RIP-oN 3). These reports will consider the definition of nanomaterials under REACH and whether nanomaterials should be treated and registered separately to the bulk form, although these projects have not yet reported (Massey, 2011 pers comm.).

6.2 Key Requirements Necessary to Evaluate Risks of Using Iron NPs for Remediation in Order to Permit their Use

New process based remediation techniques have historically encountered significant market barriers and required verified field based performance data to gain widespread regulatory and market acceptance. It is not unusual for such evidence to be demanded by regulators for specific conditions encountered or perceived in their country. Given the heightened perception of potential risks from NPs in the environment, as well as the limited evidence base related to iron NP use in the field - particularly for modified forms - it is likely that a higher burden of proof will be required by regulators prior to licensing iron NP based *in situ* remediation techniques, compared with other *in situ* remediation techniques. Within the UK the organisation CL:AIRE was established primarily for the evaluation and proving of new technologies with the aim of gaining greater UK regulatory and market acceptance. This approach has facilitated and built confidence in stepwise progression from laboratory, to large scale controlled bench-top and controlled field-scale testing. Nevertheless, new technologies such as the field application of iron NPs are likely to encounter higher scrutiny than more proven technologies.

The UK has a mature policy and practice in the risk based remediation of land affected by contamination. Most remediation is carried out through the redevelopment of previously developed land and some under Part 2A of the Environmental Protection Act 1990. Both these routes bringing about remediation is based on risk assessment established through source-pathway-receptor pollutant linkages. The last decade has seen increasing encouragement to adopt process based remediation instead of traditional civil engineering or hydraulic containment techniques.

We have used the concept of pollutant linkages to evaluate the potential risks from iron NP use *in situ* and identify the key information requirements that might be necessary for permitting their use. In this source-pathway-receptor model a significant risk occurs when an iron NP source could harm an identified receptor based on the existence of an exposure pathway joining the two. Table 7 summarises the potential pollutant linkages that might occur through iron NP use for *in situ* remediation and comments on them.

Table 7 Pollutant Linkages Representing Possible Exposure Routes for Iron NPs used in Soil and Groundwater Remediation.

	Source	Pathway	Receptor	Comments
1	Iron NPs: *handling and transportation*	Air	Human health	Potentially significant - regulated under health and safety provisions
2	Iron NPs: handling and transportation	Dermal / Ingestion	Human health	Potentially significant - regulated under health and safety provisions
3	Iron NPs powder / slurry Mixing and application	Air	Human health	Potentially significant - regulated under health and safety provisions
4	Iron NPs powder / slurry Mixing and application	Dermal / Ingestion (direct)	Human health	Potentially significant - regulated under health and safety provisions
5	Iron NPs powder / slurry Mixing and application	Dermal / Ingestion (direct)	Ecology	Potentially significant - control regulated through human health and safety provisions
6	Injected sub-surface iron NPs	Dermal / Ingestion via aquifer – controlled waters receptor	Human health	Seen as an unlikely scenario given use at depth and dilution through an aquifer
	Injected sub-surface iron NPs	Dermal / Ingestion via aquifer – controlled waters receptor	Ecology and natural soil and water microbial processes	Potentially significant, limited duration and extent to an already severely impacted zone
8	Injected sub-surface iron NPs	Soils – Plant uptake	Ecology	Seen as an unlikely scenario given use at depth in the saturated zone
9	Injected sub-surface iron NPs	Soils – Plant uptake –dermal / ingestion	Human health	Seen as an unlikely scenario given use at depth in the saturated zone

There are two potentially significant groups of risks. The first relates to risks faced by remediation process operators. These are health and safety issues which should be flagged in any permitting guidance with signposting to the appropriate regulatory regime. The second relates to potential impacts on ecology in the subsurface and controlled waters should iron NPs “breakthrough” from ground to surface water. Given that all remediation techniques impact the subsurface ecology drastically (e.g. by changing one

or more of redox potential, pH, temperature, aquifer flow, contaminant accessibility and availability, substrate availability) it may be viewed as disproportionate to regulate iron NP use based on its impacts on subsurface biology; a requirement not made of any other *in situ* remediation technique. Hence, one pollutant linkage remains where there may be a significant possibility of harm, which relates to impacts on surface water biology, should iron NPs migrate from groundwater treatment to surface water. This pollutant linkage is illustrated in Figure 9. Figure 9 differentiates between iron NPs directly injected into the subsurface and those that might be partially constrained (e.g. within a partially contained barrier). As iron NPs in the subsurface are not volatile, the primary transport mechanism in the pathway will be via aqueous advective dispersion. The remainder of these sections reviews the components of this pollutant linkage and the consequent information requirements needed for the regulation of *in situ* use of iron NPs.

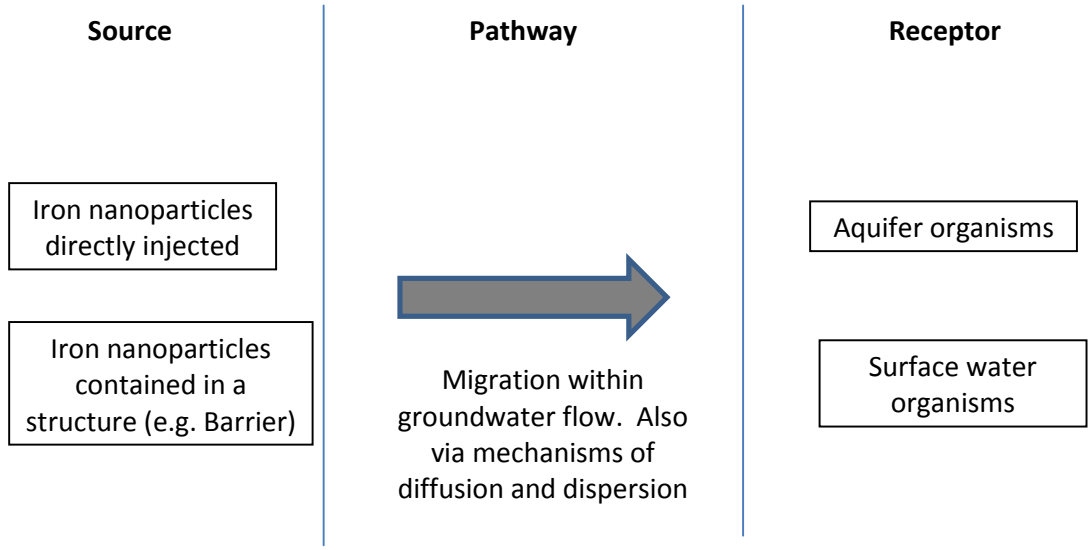

Figure 9 Conceptual Model for the Potential Impacts of Iron NP use *In Situ* for Remediation on Surface Waters

6.3 Checklist of Requirements

For iron NPs to be deployed at any individual site, consideration needs to be paid to the controllable parameters discussed individually under 'source' (Section 5.2), 'pathway' (Section 5.3) and 'receptor' (Section 5.4).

Suggested regulatory requirements of the technology service provider specifically for iron NPs are listed in Table 8. These must be supported by an adequate independently reviewed evidence base, which may reference generic technical information. Table 8 excludes permitting issues that are generic for *in situ* remediation technologies.

A rigorous pollution prevention position would be that after remediation there should not be a significant perturbation in nano scale iron oxides in the treated aquifer, and that aquifer redox and pH conditions should return to background. It may be necessary for a certain recovery period to be allowed for. A problem may well be that suitable

background comparisons cannot be found, for example if the original pollution being treated had a defining influence on aquifer conditions.

The expected life-span of the iron NPs deployed will be an important consideration in permitting. Ideally deployment should be designed so that after a defined period from the completion of remediation, unreacted iron NPs are no longer present in the subsurface or sufficiently inactivated by precipitates.

Table 8 Checklist of Permitting Issues Specific to the Use of Iron NPs

Licensing	Site Working Plan
* Type of iron NP and hazardous properties of the iron NP and any amendments used (doping metals, coatings, emulsification or other agents), in particular for surface water organisms * Types of deployment approaches used * Likely iron NP migration * Likely iron NP persistence * Likely fate of iron NPs and any amendments * Deployment risks (with appropriate cross reference to health and safety regime) * Likely maximum dispersion of iron NPs under a range of standardised aquifer and groundwater conditions	* Deployed mass * Site specific application / deployment approach * Appropriate cross reference to health and safety regime * Aquifer and groundwater conditions: composition of the soil matrix, porosity, hydraulic conductivity, groundwater gradient and flow velocity, depth to water table, and geochemical properties (pH, ionic strength, dissolved oxygen, ORP, and concentrations of nitrate, nitrite, and sulphate). * Distance of surface water receptors * Qualitative risk assessment based on type, longevity and mass of NPs deployed, standardised aquifer conditions and distance to surface water.

6.4 Types of Sites that Should not be Considered for NP Release

Sites will, certainly in the early days of using iron NPs, require a higher degree of site characterisation than is usual, or even usually expected, at the present time. An adequate understanding of the subsurface conditions is a prerequisite to ensuring the iron NPs reaches the contaminant and does not migrate to places it could adversely impact. Karn *et al.* (2009) provide a succinct summary of the issues to be considered: "*Nanoremediation, particularly use of iron NPs, has site-specific requirements that must be met in order for it to be effective. Adequate site characterization is essential, including*

information about site location, geologic conditions, and the concentration and types of contaminants. Geologic, hydrogeologic, and subsurface conditions include composition of the soil matrix, porosity, hydraulic conductivity, groundwater gradient and flow velocity, depth to water table, and geochemical properties (pH, ionic strength, dissolved oxygen, ORP, and concentrations of nitrate, nitrite, and sulfate). All of these variables need to be evaluated before nanoparticles are injected to determine whether the particles can infiltrate the remediation source zone, and whether the conditions are favourable for reductive transformation of contaminants. The sorption or attachment of nanoparticles to soil and aquifer materials depends on the surface chemistry (i.e., electrical charge) of soil and nanoparticles, groundwater chemistry (e.g., ionic strength, pH, and presence of natural organic matter), and hydrodynamic conditions (pore size, porosity, flow velocity, and degree of mixing or turbulence). The reactions between the contaminants and the iron NPs depend on contact or probability of contact between the pollutant and nanoparticles (U.S. EPA 2007)". (Karn *et al.* 2009)

7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Take Up and Benefits of Nano-Remediation

In the UK, and indeed worldwide, the majority of remediation work is based on excavation and removal or containment, although the role of landfill is slowly diminishing. Process based technologies (exploiting biological, chemical, physical solidification / stabilisation and thermal) technologies are employed, but still only on a minority of projects. Process based technologies have their greatest market penetration for problems where excavation and removal is not feasible and an *in situ* solution is necessary, in particular for treatment of contaminated aquifers.

Iron NPs are anticipated as having two major benefits for process based remediation, at least in theory, extending the range of treatable contaminant types, and increasing the efficacy of treatment (speed and degree of completion). To date the use of iron NPs in remediation in practice is largely a niche application for chlorinated solvents in aquifers, competing with more established techniques such as *in situ* bioremediation, chemical oxidation and ZVI. Nearly all practical applications have used unmodified iron NPs, with just a few cases using iron NPs modified in some way to improve stability or mobility. As stated in section 1.4, due to this lack of field experience a detailed understanding of modified iron NPs performance or possible unintended consequences (i.e. transport beyond desired treatment zones, etc.) is not attainable at this juncture without additional studies and therefore the conclusions of this study refer to unmodified iron NPs on which there is a greater evidence base. The majority of iron NP applications have taken place in North America, with a small number of applications in the field in mainland Europe (e.g. in the Czech Republic) and none in the UK. With this in mind the European Commission Directorate of Research has asked for proposals for “large scale integrating projects” to promote the exploitation of nano scale processes in remediation, with a view to projects commencing at the end of 2012. The view of UK practitioners about the likely importance of iron NP use in remediation in the UK is somewhat ambivalent from those asked during this project. However, major research investments have and are taking place in the UK and many other countries because of the anticipated advantages of the high reactivity and catalytic properties of iron NPs.

The overall conclusion of this report is that nano-remediation may offer advantages in some applications, but will be one of a wide range of possible *in situ* remediation tools, and the possible particular benefits of nano-remediation will be highly dependent on site specific circumstances.

7.2 Regulating the Use of Nano-Remediation

New process based remediation techniques have historically encountered significant market barriers and required verified field based performance data to gain widespread regulatory and market acceptance. It is not unusual for such evidence to be demanded by regulators for specific conditions encountered or perceived in their country. Given the heightened perception of potential risks from nanoparticles in the environment, as well as the limited evidence base related to iron NP use in the field - particularly for modified forms - it is likely that a higher burden of proof will be required by regulators prior to licensing iron NP based *in situ* remediation techniques, compared with other *in situ* remediation techniques.

Although most laboratory studies and subjective practitioner experience would suggest that adverse effects would be minor, localised and short-lived, there is a knowledge gap

regarding evidence of distances the particles can travel (whilst active) within the subsurface.

An intermediate step between the laboratory and implementation required before licensing might be tests at realistic scales carried out in contained experiments. This is not without precedent. For example the VEGAS facility at the University of Stuttgart in Germany can assess remediation technology in large tanks at scales of up to tens of metres[8]. In the UK the SABRE project[9] investigated *in situ* source zone bioremediation in the field using cells contained by sheet piling where contaminant and treatment chemical escape into the wider environment was prevented.

As a first step, a consensus is needed about the possible ranges of reactivity, migration potential and outcomes that might be expected in the field and which could assist the design of any scale-up work and the regulatory decision making needed to support it. The tentative findings of this review are that maximum migration will be in the order of tens of metres from injection points for modified iron NPs, with persistence of reactive iron NPs unlikely to last beyond six months to a year. These figures will be substantially less for unmodified iron NPs. However, the lack of validated field scale performance information does take these tentative extrapolations into the realms of opinion. An expert elicitation workshop would be an important step towards finding a shared opinion and as a more confident basis for planning and regulating larger scale test work. Experts, potentially including researchers and nZVI practitioners beyond the UK, can be asked to share opinions about best and worst case scenarios, their probability and the shape of any probability curve between these two points. Stochastic probability modelling can then be used to provide a basis on which risk assessment (for regulation and experimental planning) can be developed. Group consensus may pave the way for direct trials of iron NP use, depending on the degree of rigour in a risk assessment and the information and opinions of the expert group.

A further workshop task might be to prioritise the information gaps, and consequent research needs, identified in this report. This can then provide a shared set of priorities about which areas of applied research are critical for improving the regulatory landscape required to permit UK field trials and inform the global knowledge base.

7.3 Information Gaps and Research Needs

This report supports the research needs identified by Otto (2010) and shown in Table 9, but places a stronger emphasis on field based research or research carried out at field-relevant scales.

Currently, site specific consequences of iron NP applications are still hard to predict due to a lack of consequence studies, particularly in the field. The reactive (non-passivated) half-life of iron NPs in the subsurface is a current and important topic of speculation within the literature. Related to this, and a known lack of effective particle monitoring technology, remains the critical question with an absence of evidence regarding corroborated distances the particles can travel (whilst active) within the subsurface providing a priority area which requires attention. This knowledge gap is all the more pressing as its

[8] VEGAS testing facility at the University of Stuttgart:
http://www.iws.uni-stuttgart.de/institut/zwischen_lehrstuhl.en.php?Typ=Ausstattung&Abteilung=7

[9] SABRE Project testing facility:
http://www.claire.co.uk/index.php?option=com_content&task=view&id=53&Itemid=47

resolution would provide a considerable branch of assurance should it confirm the rapid reactivity and passivation suggested through laboratory experiments and from experienced field practitioners.

Other recommended studies of the consequences of nZVI use would require an intensive scheme of monitoring and analysis for the development of a sounder understanding. However this needs to be done in a comparative study bearing in mind the fate, transport and toxicity properties of the contaminants that iron NP are being deployed to treat.

Specifically, such studies would include:

- Determination of the reaction products and model reactions of mobile nano-iron particles to assess any possible unintended secondary effects on environment and ecosystem;
- Development of analytical methods for routinely determining the fate of nano-iron particles and naturally occurring background colloids or nano-sized particles in the native groundwater;
- Evaluation of the functional life-time of nano-iron particles under various representative field conditions
- Sustainability appraisal of iron NP application case studies;

Table 9 Research Needs (based on Otto 2010)

- Technology Implementation
  - Improving the nanomaterials (stability, mobility, reactivity, reducing toxicity by design). Specifically more information on product lifecycle analyses, manufacturing methods (& properties characterization) and storage periods (& their effects)
  - Fine-tuning the field application
  - Introduction of more robust quality assurance and quality control guidelines for iron NP manufacturers

- Toxicology
  - Potential health and environmental effects of the spectrum of iron NP products (includes bare iron, bimetals, and surface-modified irons)
  - Potential effects on soil microbial populations

- Fate, Transport, Transformation
  - Detecting nanoparticles in environmental media
  - Determining concentration of nanoparticles
  - Assessing the timeframe over which iron NPs remain a viable electron donor in the field and the key factors which influence this,
  - Measuring valence state of iron and importance of passivation on risk. This should include collating iron speciation data from injected particles to be reported through peer reviewed journals.
  - Measuring distance travelled in groundwater
  - Monitoring transformation and controls on reaction products

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ANNEX 1 VIEWS OF UK PRACTITIONERS

Table 1. UK Company Survey Respondents

a. ERS	f. Sirius
b. ERM	g. Taylor Wimpey
c. RAW	h. URS Corporation
d. RSK	i. Worley Parsons
e. Shell Global Solutions	

1) Is your company considering using iron nanoparticles for contaminated land remediation imminently or in the near future (next six months)?

a. Not imminent- medium to long term plans

b. No not in UK, but we have used them in the US on 4 separate occasions, all to treat TCE plume source areas

c. No

d. We haven't got any project where iron nano particle will be required in the near future. However, we have just looked into two projects (doing a Remediation Options Appraisal) where we considered the used of iron (not necessarily nano particle) as a stand-alone or combined with organic source as a potential alternative for remediating chlorinated solved and some metals. In one of them nanoparticle could potentially be beneficial if solvents are proved to be present within a less permeable strata and working as source to groundwater.

e. No

f. No

g. No

h. No

i. No

2) If not, how far in the future would you estimate it would be until use iron nanoparticles for the remediation of soil and groundwater (e.g. 1, 3, >3+ years)?

a. 1-3 years

b. The next application of nZVI will probably take place in 2012 (in US) we don’t have any anticipated use in the UK at present

c. >3 years

d. Hopefully 1 year

e. They are not relevant to the bulk of the sites we remediate (TPH-type substances). May change if chlorinated ethenes identified.

f. 2-3 years

g. If we are seeking to buy a site where iron nanoparticles are an appropriate technology, that is acceptable to the regulators and meet our internal requirements, then we would be happy to commission a contractor to use the technology. No such site is on the horizon at this point

h. Not in the near future: would suggest at least three years, probably more

i. Difficult to say but we would expect >3 years as with all new technologies there are issues around proving effectiveness and acceptance by both regulators and clients alike

3) What are the main factors behind your view and your company's position (positive and negative)??

a. Don't really have a position at present

b. nZVI has its advantages and disadvantages, and should be applied on a site-specific basis. Agglomeration of nZVI particles occur extremely rapidly after entering a natural aqueous environment, and it is difficult to quantify the potential secondary chemical reduction effects. There may be biological effects to local microbial populations, but we are not aware of any research that has been able to identify either short or long term effects and separate them from the effect of the extremely reducing environment created by the nZVI

c. It is an interesting technology and we would possibly consider its use in the future or if a contaminant which is known to be readily treatable with the technology is encountered on one of our sites. However, our understanding is that iron nanoparticles have scope for application to treat a limited number of contaminants and there is still much research to be completed on this technology regarding the efficacy, environmental fate and safety. We would anticipate much of this information will take more than 3 years to be reported. In addition, the large proportion of RAW business is oil spill related for which iron particles are not known to be greatly effective compared to other treatment technologies, so our use of this technology would be intermittent (e.g. TCE, chlorinated, chromium)

d. As for any other remedial technique we don't see nanoparticles as a solution for every site (where, for example, iron is an alternative). Clear understanding of whether nanoparticle provides better results when compared to "micro" particles (and cost benefit) is needed. I believe it could benefit sites where contaminant migration (and its remediation) is diffusion limited.

e. Not relevant to our processes/contaminants
Existing (microbial) remediation seen as better option for most of our sites
Uncertainty over health/environmental impact of nano-metals

f. The practical reason is that we do not know of any sites on which we may be working over the next year or so at which the treatment would have potential

applicability, whether alone or in combination with other approaches. That is due both to the risk drivers and contaminant mixtures present. Certainly, the process has attractions, particularly: (a) if it can be applied as a "one-shot" treatment as an alternative to chemox or in situ bio, say; or (b) if cost and regulatory issues make it more attractive than considering a PRB

g. We would consider the commercial, technical, environmental and social risks, opportunities and benefits as we would for any other technology. There is often some reluctance in commercial terms to be a pioneer, but we have been in the past (e.g. six phase heating, chemical reduction, steam etc)

h. Authorisation and acceptability, need for demonstration of no significant environmental, health or safety issues associated with release, costs, need for more published guidance, practicability issues in terms of implementation and overall technical effectiveness in the field as opposed to laboratory or pilot scale studies. This is the case both in the UK and continental Europe, including Germany and Italy where there is already difficulty in applying 'consolidated' technologies such as ISCO due to the authorisations needed. Additionally in Germany, based on previous laboratory tests, there appeared to be an issue with the stability of nano-scale ZVI (URS found evidence for clogging of the nano-scale particles if ZVI is not "fresh"), which resulted in reduced efficiency. There was also an issue with distributing ZVI in the subsoil/saturated zone potentially related to rapid adsorption or clogging. The project team was not in a position to further investigate this, and the testing concluded that ZVI was less efficient than permanganate.

i. See answer above - many of our UK clients have also secured landfill tax exemption to March 2012 and therefore this will drive remediation activities over the next 12-18 months

4) What barriers do you consider are presently inhibiting iron nanoparticle use in remediation?

a. Ignorance; uncertainty regarding the regulatory position

b. Similar or the same barriers inhibit any amendment that is utilized as an injected in situ remediation amendment. Achieving contact between the amendment and the target compound is difficult under field conditions. Optimizing distribution and contact is a challenge, especially when the product is so expensive. The cost of nZVI can be prohibitive to larger scale application of this product

c. Safety
Environmental fate
Efficacy / range of contaminants that can be treated
Regulatory issues

d. Behaviour (fate and transport) once injected in groundwater. Understanding potential for secondary reactions and risks to controlled waters/ecosystem? Risks to human health when handling (dermal, inhalation issues?), How effective are PPEs??

e. Lack of underpinning science on health/environmental effects, and fate/transport (which impacts regulatory position and confidence of remediation)

f. Limited awareness of its range of applications (contaminants, ground conditions); limited understanding of regulatory position; lacking robust cost information. I would also mention that I am not aware of technology suppliers who are marketing it heavily to consultants/remediation contractors (compare the amount of marketing done on in situ bio, S-S, chemox, etc.).

g. More research is needed to understand the fate and transport of free nano-scale materials in the environment, their persistence and toxicology, and whether the theoretical benefits of nano-scale materials can be realized in commercial terms

h. Regulatory issues, restricted track record of application and demonstration of technical effectiveness in field scale projects, demonstration of no untoward effects on health or environment, practicability issues in terms of application, cost effectiveness

i. Combination of lack of track record, issues with delivering of nanoparticles to the contaminant, regulator acceptance/buy in, cost efficiency

5) What experience of nanoparticle remediation has your company (i.e. not necessarily iron-based), be it laboratory-based, PhD sponsorship, or experience of an overseas office?

a. We have used ZVI in numerous applications and I am looking at the potential for nano-scale injections, but it's early days

b. Experience to date is overseas (Belgium/USA) in UK we have only used micro scale iron. In the USA we have used Z-Loy and a product called PolyMetallix, a nZVI manufactured by Polyflon, a wholly owned subsidiary of Crane Co. located in Norwalk, Connecticut. We have applied nZVI in a dry well source area to treat TCE. PolyMetallix exhibits an average particle size of ~50 nM. Z-Loy, as a colleague has indicated, exhibits an average particle size of ~200 nM. Z-Loy has been used to treat a source area with concentration of mixed chloroethanes and chloroethenes in excess of 100 mg/L

c. Research project sponsorship / supervision (MSc - Lancaster) entitled "Investigation into the Remediation of Hydrocarbon Contaminated Groundwater Using Multi-Scale Activated Carbon

d. As far I am aware we haven't had the opportunity to use or deal with nano particles to date

e. Keep a watching brief on scientific literature. Not funding research on nano-remediation at present

f. Nothing on nanoparticles beyond keeping a watch on developments

g. No experience to date

h. Germany: Project information for the works referred to in Q.3 is attached: Australia: Newcastle, NSW, Australia: a field trial for the injection of 70 micron-

scale ZVI and liquid ferrous chloride is being conducted for the in situ geochemical fixation of arsenic in groundwater by our Sydney office, but they are currently not considering nano scale iron at this stage. France: Carouge, France: URS examined the potential for injecting nano scale iron for the remediation of a chlorinated solvent issue in groundwater but ruled it out on grounds of cost and the difficulty of injection (High pressures required versus low penetration into the formation). USA: Dr. Anna Hovsepyan, a Senior Environmental Engineer in the Gaithersburg, MD (USA) office of URS Corporation has been collaborating with the University of Florida on research that evaluates the safety and toxicity of nanomaterials and their impact on the environment and has assisted in the development of a new graduate level course in Environmental Nanotechnology

i. Worley Parsons has not used iron nanoparticles to date however we remain open to assessing this option as part of our usual remedial options appraisal process on a site specific basis

ANNEX 2 IRON NANOPARTICLE CASE STUDIES

Overview Table of Global Iron Nanoparticle Field Applications

Location	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	Nano Particle Type	Volume of Nano particle	Ref
Bornheim, Germany	Full	Sandy gravel		PCB, TCB, PCE, TCA, Pesticide, solvents, perchlorates		Sleeve-pipe injection	nZVI, ZVI	nZVI (1000 kg) and ZVI (2000 kg)	1
Horice, Czech Republic	Full	Low permeable aquifer		PCE (TCE, DCE)	70mg/l	High pressure pneumatic injection	nZVI (RNIP and NANOFER)	2x 1 tonne	1
Pisecna, Czech Republic	Full	Sandy / Silt	GW	Chlorinated Ethenes		High pressure pneumatic injection	nZVI	3 x 1.5 tonnes of RNIP and NANOFER	1
Spolchemie, Czech Republic	Pilot	Porous Aquifer	GW	Chlorinated Ethenes		Infiltration Wells	Fe (B)		1
Kurivody, Czech Republic	Pilot	Fractured Bedrock	GW, overburden, weathered bedrock	Chlorinated Ethenes		Infiltration Wells	Fe (B), RNIP		1
Piestany, Czech Republic	Pilot	High Permeable Aquifer	GW	Chlorinated Ethenes		Infiltration Wells	Fe (B)		1
Permon, Czech Republic	Pilot	Fractured Bedrock	GW	Cr(VI)		Infiltration Wells	RNIP		1
Rozmital, Czech Republic	Pilot	Fractured Bedrock	GW	PCB		Infiltration Wells	RNIP, Nanofer		1
Hluk, Czech Republic	Pilot	PRB filter	GW	Chlorinated Ethenes		Infiltration Wells	RNIP, Nanofer		1
Uhersky Brod, Czech Republic	Pilot	Porous Aquifer	GW	Chlorinated Ethenes		Infiltration Wells	Nanofer		1

Location	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	Nano Particle Type	Volume of Nano particle	Ref
Uzin, Czech Republic	Pilot	Low permeable aquifer	GW	Chlorinated Ethenes		Infiltration Drains	Nanofer		1
Brownfield, SK, Canada	Pilot	Unconsolidated sediments	Soil	TCE, DCE		N/A	N/A		1
Biella, Italy	Pilot	Porous Aquifer	GW	TCE, DCE		Gravity Inflitration	nZVI		1
Thuringia, Germany	Pilot	Porous Aquifer	GW	CAH, Ni, Cr, NO_3		Injection Wells	nZVI		1
Hannover, Germany	Pilot	Chemicals storage facility	Soil and GW	CHC, BTEX. HC		Aqueous Slurry	N/A		1
Schönebeck Germany	Pilot	Porous Aquifer	GW	VC		Push Inflitration	RNIP		1
Asperg, Germany	Pilot	Fractured rock	GW	Chlorinated Ethenes		Sleeve-pipe injection	RNIP		1
Gaggenau, Germany	Pilot	Porous Aquifer	GW	PCE		Sleeve-pipe injection	RNIP		1
San Fransisco Bay, CA	Full	Course alluvial silt clay sediments	GW	PCE, TCE		Multi-level Push-Pull	nZVI		1
Valcartier Garrison, Canada	Full	Alluvial sands and gravel, glacial sands, silts and gravels	GW	TCE, 2-DCE, cis-1,		Push Injection / closed loop recirculation	nZVI	4,500 kg	2
Lakehurst, NJ, USA	Full	Sand / gravel Coastal Plain Aquifer	S and GW	PCE, TCE, TCA, c-DCE, vinyl chloride	900 µg/L	Direct Push	BNP	1360 kg (2005) and 225 kg (2006)	3
Jacksonville, FL, USA	Full	Silt / fine sands(0-24ft) and dense clay (24-54ft)	GW	TCE, TCA, DCE, vinyl chloride	TCE (26,000µg/L); TCA (11,000µg/L); DCE (44,000µg/L)	Direct push / closed loop recirculation	BNP	135 kg	3
Patrick AFB, FL, USA	Full	Groundwater; Surficial Aquifer; fine/ medium sandy silts	S and GW	TCE (and daughter contaminants)	150,000 µg/L	High pressure pneumatic injection	Emulsified ZVI (EZVI)	N/A	3
Cape Canaveral, FL, USA	Full	Groundwater; Surficial Aquifer; fine/ medium sandy silts	S and GW	TCE	439,000 µg/L	Drop Tip injection	Emulsified ZVI (EZVI)		3

Location	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	Nano Particle Type	Volume of Nano particle	Ref
Cape Canaveral, FL, USA	Pilot	Surficial aquifer with fine / medium grained sands	S and GW	TCE	N/A	High pressure pneumatic injection and pressure pulse enhanced injection	Emulsified ZVI (EZVI)	61 gallons	3
Port Royal, SC, USA	Pilot	Sandy soils (15 different types)	S 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)	Direct Push and pneumatic injection	Emulsified ZVI (EZVI)	935 gallons	3 (ESTCP Report)
Santa Maria, CA, USA	Pilot	Interbedded sands, silts and clays (bedrock encoutered)	GW	TCE, DCE	TCE (2.5 mg/L)		BNP	30g/L of nZVI slurry	3
Phoenix, Goodyear, AZ, USA (Phase I)	Pilot	Alluvial deposits of western Salt River Valley. Consisting of upper alluvial unit, middle fine grained unit, lower conglomerate unit and groundwater at 85 ft	GW	TCE, PCE, perchlorate	39,000 µg/L	Injection Wells	nZVI	10,400 litres of a 2.1ug/L nZVI slurry (total of 24 kg)	3
Phoenix, Goodyear, AZ, USA (Phase II)	Pilot	Alluvial deposits of western Salt River Valley. Consisting of upper alluvial unit, middle fine grained unit, lower conglomerate unit and groundwater at 85 ft	GW	TCE, PCE, perchlorate	3,500 to 11,000 µg/L	Injection Wells	nZVI		3
Edison, NJ, USA	Pilot	Fractured brunswick shale bedrock and 4-6ft of silt and clay soil	Fractured Bedrock	TCA, TCE, DCA, DCE, cholorethane, vinyl chloride	TCA (37,000mg/L); TCA (10,000µg/L)	Injection Wells	nZVI	300 lbs nZVI; 1,500 gallon emulsified vegetable oil	3
Passic, NJ, USA	Pilot	Soils consisting of highly permeable sands (0-20ft); silt (20-26ft)	GW	TCE	450 - 1,400 µg/L	Pneumatic Fracturing Injection /	nZVI	108lbs of nZVI; 1,200 lbs of emulsified oils	3

Location	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	Nano Particle Type	Volume of Nano particle	Ref
						Hydraulic Injection		injected into 3 points	
Research Triangle Park, NC, USA	Pilot	Triassic Basin Sandstone interbedded with siltstone grading downwards into mudstones	GW in fracture bedrock	PCE, TCE, DCE, VC	14,000 µg/L	Injection Wells	BNP	1.9 µg/L of BNP slurry (total volumer of 6,056L	3
Salem, OH, USA	Pilot	Glacial till over fractures sedimentary bedrock	GW in fracture bedrock	PCE, TCE, DCE, VC	100,000 ug/L	Injection Wells	nZVI	10-20g/L nZVI slurry (total volumer of 70 kg)	3
North Slope, Prudhoe Bay, AK	Pilot	Organics over alluvial gravels	S	TCA, diesel fuel	TCA (58,444 ug/Kg)	Pressurised Injection	BNP	N/A	3
Rochester, NY, USA	Pilot	Glacial till overburden overlying fractured sedimentary bedrock	GW in bedrock	Methylene chloride, 1,2-dichloropropane, 1,2-dichloretheane	500,000 ug/L	Gravity Feed Injection	nZVI	10-20g/L nZVI slurry (total volumer of 100 kg)	3
Rockaway Township, NJ, USA	Pilot	Organics rich soil	GW	Carbon tetrachloride, TCE	CCL4 (250 ppb); TCE (87 ppb)	Injection Wells	nZVI	120 lbs of nZVI over 2 wells	3
Quebec, Canada	Pilot	deltaic and proglacial sands	Sands and clayey silts	TCE, DCE, VC	TCE (300 ppb); DCE (50 ppb)	Injection Screen Wells	nZVI	4,550 kg of nZVI and BNP mixed with soy proteins	3
Ringwood, NJ, USA	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	3
Hamilton Township, NJ, USA	Full	Middle Potomac Raritan Magothy (MPRM) Aquifer	GW	TCE, DCE, TCA, DCA	400 - 1600 µg/L	Push Injection (2 Phases)	Nanoiron slurry (NanoFe Plus ™)	2000 kg	3
Rochester, NY, USA	Full	Glacial till over fractures bedrock	GW, overburden, weathered	TCE	1900 µg/L	High pressure pneumatic injection	nZVI		3

Location	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	Nano Particle Type	Volume of Nano particle	Ref
			bedrock						
Alameda Point, CA, USA	Pilot	N/A	GW	TCE	1,600 µg/L	Direct Injection			3
Palo Alto, CA, USA	Pilot	Groundwater; multiple water bearing units; sand and gravel zones separated by low-permeability clays	N/A	PCE, TCE, Freon	PCE (26,000 µg/L); TCE (70,000 µg/L);	Injection Wells			3
Sheffield, AL, USA	Pilot	Unconsolidated sediments	GW	PCB's, PCE, TCE, DCE, VC	10,000 - 24,000 µg/L	Gravity Feed Injection			3
Winslow Township, NJ, USA	Pilot	Unconsolidated sediments	GW	PCE, TCE, DCE	TCE (3,000 µg/L)	Gravity Feed Injection			3
Trenton, NJ, USA	Pilot	Shallow Aquifer (7-25ft)	S and GW	PCE, TCE, c-DCE, vinyl chloride, chloroform, carbon tetrachloride, 1.1-DCE	TCE (pre injection of 445 - 800 µg/L) (MAX: 4600 µg/L)	Gravity Feed Injection			3
Northern Alabama, AL, USA	Pilot	N/A	S and GW	PCE, TCE and PCB's	TCE MW-1 (1655 ppb) MW-2 (2710 ppb)	Gravity Feed Injection			3
Rock Hill, SC, USA		Unconsolidated sediments	GW	TCE, DCE			nZVI		4
Industrial Site, Ontario, Canada		Unconsolidated sediments	GW	PCE, TCE	TCE 86,000 µg/L		nZVI		4
Hampton, SC, USA		Silty to fine sand from 25 - 45 feet bgs - then dense clay	GW	TCE, PCE	TCE 300 ppm		nZVI		4
Mechanicsburg, PA, USA		Fractured rock	GW	TCE			nZVI with Pd		4
Kaiohsiung, Taiwan		Medium - coarse sand unconfined aquifer, 4-	GW	TCA, TCE, DCA, DCE, Vinyl chloride	VC 4,562 µg/L, EDA 207 µg/L, DCE		nZVI		4

Location	Scale	Geology	Media treated (S - Soil, GW - Ground water)	Contaminant Treated	Contaminant Concentration	Injection Technique (Technology Design)	Nano Particle Type	Volume of Nano particle	Ref
		18m bgs			1,151 µg/L, TCE 682 µg/L				
Titusville, PA, USA				PCE, TCE, cis-DCE			nZVI		4
Frankling Square, NY, USA				PCE, TCE, 1,1,1-TCA, Cr(VI)			nZVI		4
State College, PA, USA				Pesticides (DDE, DDT)			nZVI		4
Newfield, NJ, USA				TCE, cis-DCE, Cr(VI)			nZVI		4
Hamilton Landfill, NJ, USA				1,1,-TCA, 1,1-DCA, 1,1-DCE, Pb, Ni			nZVI		4
Kearny, NJ, USA				Cr(VI)			nZVI		4
Aberdeen, MD, USA				1,1,2,2-TeCA, 1,1,1-TCA, TCE, Cr(VI)			nZVI		4

References:

1) Müller and Nowack (2010)
2) Golder Associates (2009)
3) US EPA (2008), Selected Sites Using or Testing Nanoparticles for Remediation
4) US EPA (2009) Supplemental Material: DOI (http://dx.doi.org/), record: 10.1289/ehp.0900793.S1

Case Study Example 1: Naval Air Station Jacksonville, Florida

Site Details

Location: Naval Air Station Jacksonville, Florida, USA.
Scale: Full Scale
Pollution Type: Two underground storage tanks (USTs) that had received waste solvents.
Nano Particle Type and Volume: The particles are Bi-metallic Nano-scale Particles (BNP) and consisted of 99.9% iron and 0.1% palladium and polymer by weight.
Dates: January 2004 – 2010.
Regulatory Issues: This demonstration project was conducted under the oversight of regulatory personnel from the Florida Department of Environmental Protection (FDEP) and the United States Environmental Protection Agency (U.S. EPA) but with minimal regulatory permit requirements and constraints.

Geology & Media Descriptions

Geology: Silty to fine sand from 0 to 24 feet bgs; dense clay from 24 to 54 feet bgs
Media Treated: Groundwater

Target Media

Contaminant Treated: Max TCE: 26,000 µg/L; Max TCA: 11,000 µg/L; Max DCE: 44,000 µg/L. These contaminant concentrations indicate the potential presence of DNAPL.

Volume of Treated Media

The horizontal extent of contamination is approximately 1,450 ft^2 with a thickness of 18 ft (saturated zone), resulting in a total volume of 967 yd^3 of soil. The estimated mass ranges between 42 and 125 lb with the statistical average mass centred at 61 lb.

Application Methodology

Implementation:
Bench-scale treatability testing indicated that the application of nZVI could degrade chlorinated organics present at the site with removal efficiency between 96 and 98% with an applied iron concentration of 1.25 to 13.75 g/L. Test results indicated that generation of undesirable daughter products (i.e., DCE and VC) from the reduction process was insignificant (TtNUS, 2003a).

Injection Technique (Technology Design)
NZVI was emplaced using two mechanisms: (1) strategic direct-injection into known “hot spots” using direct-push technology (DPT), and (2) a “closed-loop” recirculation process (Tetra Tech, Inc. 2005). Direct injection of the nano-scale iron using DPT was employed first at 10 “hot spot” locations. A recirculation system was used to distribute the nZVI in the rest of the suspected source zone.

Number of Injections

The design of the recirculation system consisted of four injection and three extraction wells, including two existing injection wells for the initial nZVI injection. Because the viscosity of the nZVI suspension is similar to groundwater (due to the low iron concentration) the water was introduced into the aquifer via gravity flow only. Injection pipes had drilled slots to allow discharge of the iron into targeted depth intervals that were characterized to have elevated contaminant concentrations.

Volume of Nanoparticle

300 lb (135 kg) of BNP was made into 4.5 to 10 g/L slurry. For injection via DPT, the iron suspension was diluted to 10 g/L and injected directly into the DPT boreholes using pumps from 7.5 to 23.0 ft bgs, equating to approximately 4.2 lb of iron injected in each borehole.

Monitoring & Evidence

Monitoring & Sampling Network
Short-term performance monitoring was conducted with groundwater samples collected within 6 weeks after nZVI injection from a select number of wells (injection wells (4), extraction wells (3) and treatment zone wells). Longer-term performance monitoring was conducted between 2 months and 1 year after injection. This phase of monitoring evaluated the longer-term performance of the remedial system in the source area and within the dissolved-phase plume.

Operation and Maintenance Requirements
The first monitoring event took place 5 weeks after the initial injection. The monitoring activities continued beyond the original planned 9 months due to the increase in TCE and DCE concentrations in certain source zone wells

Performance Detail
Results of the remedial process varied widely from well to well. The recirculation process appeared to enhance desorption of contaminants into the dissolved phase. Many wells achieved over a 65% decrease in concentrations of parent VOCs within a short period of five weeks. Some source zone wells however, experienced a rise in both TCE and DCE concentrations after injection. This likely stems from poor distribution of the BNP slurry and possible displacement of dissolved TCE.

Immediately after nZVI injection, ORP declined to approximately −200 mV. The resulting reducing conditions may have been strong enough to stimulated anaerobic biodegradation and hydrogenolysis, but may not have been strong enough to cause substantial abiotic reduction (beta-elimination). Within about 12 weeks, ORP levels rebounded considerably, indicating that the nZVI was dissipating. However, the groundwater remained anaerobic for over a year following the iron injection, indicating that conditions suitable for biodegradation continued for a substantially long time. Groundwater pH levels remained relatively unchanged throughout the demonstration, indicating that the nZVI may not have induced strongly reducing conditions suitable for abiotic reduction.

Although microbial activity can result in generation of CO_2 and a concomitant suppression of pH, there are not enough oxidised species (DO, nitrate, etc.) in the native groundwater for this effect to be significant. Therefore, some increase in pH would be expected following iron injection.

Clean Up Goals
The project was successful in achieving its clean-up goal of reducing total site contaminant mass by 40-50%.

Case Study 1 References

Naval Facilities Engineering Command (NAVFAC) (2005) Cost and Performance Report Nanoscale Zero-Valent Iron Technologies for Source Remediation

Tetra Tech, Inc. 2005. Draft Final Nanoscale Iron Injection Cost and Performance Report, Naval Air Station, Jacksonville, Florida. Prepared for Naval Facilities Engineering Command-Southern Division. July.

TtNUS. 2003a. Bench Scale Treatability Study Work Plan, Hanger 1000, NAS Jacksonville, Jacksonville, Florida.

U.S. EPA (2008) Selected Sites Using or Testing Nanoparticles for Remediation
U.S. EPA (2010) Nanotechnology Project Profiles Database (http://www.clu-in.org/products/nano/

Case Study Example 2: Horice v Podkrkonosi, Czech Republic

Site Details

Location: industrial site KAR-BOX, Horice v Podkrkonosi, Czech Republic
Scale: Full Scale
Pollution Type: Chlorinated Solvents from 5 isolated sources (e.g. storage, scrap yard)
Nano Particle Type and Volume: RNIP (laboratory experiments + pilot test); NANOFER 25S (laboratory experiments + pilot test + full scale); 500 kg nZVI (NANOFER 25S) used in three stages on the full-scale: Stage 1 (200 kg in 2008), Stage 2 (160 kg in 2009) and Stage 3 (140 kg in 2010).
Dates: Pilot test (3/2008); First stage (11/2008), Second (11/2009), Third (11/2010)
Regulatory Issues: No Water Law Exemption required for this site

Geology & Media Descriptions

Geology: Quaternary sediment (6 m) overlying Turonian sediment (10 m); Low permeability (~10-6 m/s). Fractures in underlying consolidated bedrock (NE-SW directions).
Media Treated: Groundwater; Two contaminated aquifers comprising the two named geological units in continuity with one another.

Target Media

Contaminant Treated: PCE (TCE, DCE). Max 60 mg/l Total CHC within the Quaternary aquifer); 10 mg/l within the Turonian aquifer. No evidence of DNAPL present.
Volume of Treated Media: 120 x 60 m area, with the contamination at a depth of 3-10 m.

Application Methodology

Implementation
Laboratory test (concentration dependency, kinetics with water and soil from the site) indicated that the application of nZVI could degrade Chlorinated hydrocarbons (CHC) present at the site; efficiency over 90 % with nZVI (both types) concentration over 2 g/l. Accumulation of DCE, as the major daughter product, was smaller than 10% of original CHC concentration.

Injection Technique (Technology Design)
Direct push injection without installation of permanent wells (pilot test applied to permanent wells only) at a working pressure of 0.8 MPa. 20% pre-mixed nZVI slurry was mixed with deoxygenated water immediately prior to injection. Each point comprised 4 injection horizons within a 3-10 m depth interval, with 1 m^3 of solution applied into each well and with an nZVI concentration about 2.5 g/l.

Number of Injections

The above injection technique was applied to 80 injection wells. Each point was injected 3 times throughout the treatment period (one in each Stage).

Volume of Nanoparticle

500 kg nZVI (NANOFER); Stage 1 (200 kg in 2008), Stage 2 (160 kg in 2009) and Stage 3 (140 kg in 2010).

Monitoring & Evidence

Monitoring & Sampling Network
Regular monitoring (14 days or 30 days interval throughout all post-injection monitoring); CHC, pH, ORP, dissolved oxygen measured; 25 monitoring wells (Quaternary) + 10 Turonian + 2 Cenomanian (supervisory).

Performance Detail

Reduction to 25-40% (> 90 % (in the diffuse part)) of the original contaminant concentration was achieved. In the second stage (11/2009) 160 kg of nZVI was injected. After second injection another decrease of contaminated areas was observed. Contaminated areas with total CHC concentration over 5 mg/l were reduced to 20% of the original size; areas with concentration 2-5 mg/l increased about 40% (result of the over 5 mg/l areas reduction). The final results are not yet evaluated.

DCE significant increase was observed only at wells outside of the treated region (migration of DCE). No VC increase was observed.

At a lactate pilot site the high concentration of DCE appeared and remained. A subsequent injection of nZVI at this site caused a significantly faster CHC removal compare to a single nZVI injection and this combined method is under study.

Clean Up Goals
The site limit is 2 mg/l of the total CHC.

Case Study 2 References

Müller, N. C. and Nowack, B. (2010)
U. S. EPA, 2010b (CLU-IN Webinar)
M. Cernick 2011 (pers. comm.)

Case Study Example 3: Pisecna, Czech Republic

Site Details

Location: Pisecna, Czech Republic
Scale: Pilot and Full scale (with preceding laboratory scale studies)
Pollution Type: Chlorinated Solvents – hazardous waste landfill
Nano Particle Type and Volume: 30 kg of pure iron RNIP type and 1030 kg of pure iron NANOFER 25N (uncoated) and NANOFER 25S (coated) types were introduced in three steps (2 separate field pilot tests with RNIP and NANOFER, 2 full scale applications with NANOFER only)
Dates: Field pilot tests in 2008,
1st stage of injection of 600 kg of pure iron NANOFER in 11 – 12/2009
2nd stage of injection of 400 kg of pure iron NANOFER in 08 – 09/2010
Regulatory Issues: No Water Law Exemption required for this site

Geology & Media Descriptions

Geology: Fractured Metamorphic Bedrock (Schists and Gneiss) with a permeability between 10^{-4} and 10^{-6} m/s
Media Treated: Groundwater

Target Media

*Contaminant Treated: T*CE, PCE, 1,2-cis-DCE, VC, 1,2-DCA, contaminated up to 35 m bgs.
Volume of Treated Media: 25,000 m^3 volume of contaminated aquifer. Approximately 1 tonne of chlorinated ethenes at a depth of 20-35 m below surface. Pure DNAPL found during an infiltration system installation in one well.

Application Methodology

Implementation
Laboratory testing and a pilot study were undertaken in advance of the full scale demonstration. As part of the laboratory testing 5 different types of nanoparticles, with NANOFER and RNIP selected for the full scale demonstration. All nanoparticles were tested for aggregation (DLS), sedimentation (column tests), mobility (column tests), reactivity (kinetic tests over different concentrations and measured in different time steps).

Injection Technique (Technology Design)
nZVI (type Nanofer25 and 25S) slurry prepared at the site from dry powder. The slurry was then dosed into pre-treated, deoxygenized water and injected into 30 cased wells.

Number of Injections
30 cased injection wells were installed. Additionally 7 pumping wells operated in discontinuous mode during injection and were switched off for a period of approximately 3 months after the injection period.

Volume of Nanoparticles
300 kg of 20% nanoiron slurry used for a field pilot test, a 1,000 kg of pure iron (equivalent of 5,000kg of 20% nanoiron slurry) used for full scale process.

Monitoring & Evidence

Monitoring & Sampling Network
All 30 available points sampled and analyzed twice a year with respect to chlorinated hydrocarbons. 6 selected point sampled monthly during the 6 month period after the nanoiron injection (analysed for Chlorinated hydrocarbons, dissolved inorganic compounds, pH, Dissolved Oxygen, Conductivity and Oxidation Reduction Potential.

Operation and Maintenance Requirements
For the injection process needs the technological water for nanoiron slurry dilution, The injection is provided under the pressure into 5-8 wells simultaneously. Cased wells must be screened in the appropriate interval. The knowledge of vertical distribution of contamination is very important during the injection system installation.

Performance Detail
The results of the pilot test showed a significant decrease of CHC concentration of 40-80%. The full scale remediation started at the end of 2009 and results of the application in 2010 are not yet available. After the first stage injection the rebound effect has been observed in the order of 30 – 50%.

Clean Up Goals
Target values already achieved at the majority of monitored wells, with the exception of the wells placed in the hotspot.

References

Müller, N. C. and Nowack, B. (2010)
U. S. EPA, 2010b (CLU-IN Webinar)
P. Kvapil 2010 (*pers. comm*.)